Bridging the Gap: Demonstrating the Connection Between Non-Valence Correlation-Bound Anions and Image Potential States Using a One-Electron Model

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Bridging the Gap: Demonstrating the Connection Between Non-Valence Correlation-Bound
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Devin M. Mulvey, PhD
University of Pittsburgh, 2023

This work documents progress in developing a one-electron model Hamiltonian capable of
simulating the non-valence correlation-bound (NVCB) anions of hexagonal polycyclic aromatic
hydrocarbons (PAHs) consisting of tens to thousands of atoms. The model potentials incorporate
atomic electrostatic moments, coupled inducible atomic charges and dipoles, and atom-centered
repulsive Gaussians parameterized on quantum mechanical data to describe the interaction between
the excess electron and PAH. By comparing model results to reference all-electron dipole polariz-
abilities, electrostatic, and polarization potentials we validate that our model potential components
capture the fundamental physics underlying the static and perturbation dependent properties of the
PAHs. The electrostatic and polarization models reproduce the behavior expected of graphene when
simulating the properties of large, finite molecules. By extracting the electron binding energies
(EBEs) and single particle orbitals of the NVCB anions we validate model results against equation of
motion (EOM) and random phase approximation (RPA) results. The model predicts a 1s-like ground
state and a variety of excited state NVCB anions with wavefunctions resembling the hydrogenic
2s, 2p, 3p, 3d, 4f, and 5g orbitals for PAHs ranging in size from 54 to 5400 carbon atoms. We
present results demonstrating that with increasing system size, the NVCB anions of these PAHs
evolve into the image potential states (IPSs) of graphene. Despite polarization being the primary
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Preface

“"I cannot remember the books I’ve read any more than the meals I have eaten; even so, they have made me.” - Ralph Waldo Emerson

These past five years of graduate studies have presented me with numerous opportunities, many of them scientific. However, chances for self-reflection have also arisen, much like this very moment.

So much has changed outside and within myself; yet, at times, I feel exactly as I did when I started research in Dr. Jordan’s lab in the summer of 2018: a novice scientist, perhaps a bit overconfident in their abilities, excited by the promise of what is to come. At other times, I become acutely aware of everything that is behind me and where I am now: the knowledge and skills I have gained, lost, and relearned; the colleagues who have helped shape my research and ethos as a scientist; the countless hours of encouragement, advice, and love friends and family have provided me on this singular pursuit. With the heavy lifting behind me, I now have the opportunity to acknowledge them.

First, I must express my gratitude to my mother Loriann, stepfather Guy, aunt Courtney, uncle Phil, sister Michaela, and brother-in-law Matthew. There have been times during my graduate studies when I lost faith in my abilities as a scientist, growing fearful, even defeatist, about my prospects. My family may be small in number, but they are mighty in their ability. They find physical and mental strength for me when I lack it. I struggle to summarize in words how integral their support has been in allowing me to reach this very moment. All I can say is thank you, and I love you all very much.

Unfortunately, there is one member of my family who lost their battle with cancer ten years ago. My father, Donald, was an incredibly intelligent and compassionate person. His background in electrical engineering and general enthusiasm for science intrigued me at a young age and was undeniably crucial to my choice of a career path. A core childhood memory for me is when my parents bought me a Fisher-Price chemistry set, and my father excitedly took pictures while I watched acetic acid etch tinfoil in the sun. There have been countless times during the course of my undergraduate and graduate studies that I found myself asking, "What would he think of this?" or
"Would he be proud of me?" There are so many moments I wish I could have shared with him, but I am still incredibly thankful for the time we could share.

I never fully understood the cliché saying, "Friends are the family you choose," but I have come to appreciate it in these past five years. In my first summer at Ken Jordan’s lab, two group members, Amanda and Shiv, approached my cubicle to invite me out for lunch. Unexpectedly, this simple act led to me finding some of my closest friends. In a short amount of time and many social invitations later, they had integrated me into an intelligent and hilarious group of coevals (pun intended). I am grateful to Shiv, Amanda, Rajan, Riley, Sean, Sri, and Amy for inviting me into their community and choosing me as a part of their extended family. Our in-person and virtual hangouts have enriched me both socially and intellectually, proving indispensable to my happiness over these past five years.

Last, but certainly not least, I want to acknowledge my thesis advisor, Dr. Ken Jordan. Ken has served as an incredible resource of both scientific knowledge and professional advice. He has included me in exciting interdisciplinary collaborations within and outside of my thesis work. He provided me with opportunities to mentor the research of students at various points along their educational journey. Most importantly, he has helped shape my understanding of what constitutes meaningful research and the role of an educator. I am thankful for his guidance and patience.

In summary, what I have come to realize in the past five years is that I am still that child playing with a Fisher-Price chemistry set. I am that novice scientist excited for what has yet to come. I am also the author of this thesis; proud of what I have accomplished, but also acutely aware of the growing number of things I do not understand. Even so, it is my family, friends, and colleagues that have brought me to this moment. Thank you to you all.
Molecular anions can be broken into two classes which are distinguished by the nature of the interaction between the excess electron and charge distribution (nuclei and electrons) of the molecule. There is the familiar class of valence-bound anions, where the excess electron occupies a valence orbital close to the nuclei of the system with short-range interactions stabilizing the anion. The second class is non-valence anions, where the excess electron occupies a spatially diffuse, heavily delocalized orbital with long-range interactions dominating the anion’s stability. Non-valence anions can be further subdivided by the nature of the long-range interactions. An excess electron can be bound by a permanent electrostatic moment producing a non-valence electrostatically-bound (NVEB) anion. On the other hand, if a molecule’s charge distribution readily distorts in response to the electric potential and field of an excess electron, a.k.a. polarizable, the excess electron can be bound by these dispersion-like, instantaneous fluctuations producing a non-valence correlation-bound (NVCB) anion. For many non-valence anions permanent electrostatics and dispersion-like interactions both play a role, so which category a non-valence anion falls into depends on which of the two dominates the binding.

Figure 1 shows the key features distinguishing NVCB anions from their more familiar valence bound counterparts.
Figure 1: Natural orbital, electron binding energy, and point group symmetry of lowest energy valence bound and non-valence correlation bound anion of C$_6$F$_6$ calculated via equation-of-motion second order Møller-Plesset perturbation theory (EOM-MP2). Isosurfaces of the singly occupied natural orbital of C$_6$F$_6^{-}$ are plot such that they enclose 90% of the excess electron’s charge density. Images were adapted from the following publication.$^1$

The figure shows the singly occupied natural orbital, electron binding energy, and point group symmetry of lowest energy valence bound and non-valence correlation bound anion of C$_6$F$_6$ calculated via electron affinity equation-of-motion second order Møller-Plesset perturbation theory (EA-EOM-MP2)$^{2,3}$ by Voora and Jordan.$^1$ The NVCB anion is bound much more weakly than the valence anion; in their respective ground state geometries the EBEs differ by a factor of $\sim 4$. Furthermore, the excess electron does not perturb C$_6$F$_6$ from its ground state geometry (D$_{6h}$) in an appreciable manner when bound as an NVCB anion, but the molecule’s geometry is altered considerably from its planar configurations (D$_{6h}$ $\rightarrow$ C$_{2v}$) when the excess electron is bound as a valence anion. This dramatic difference in binding energy and orbital shape is the result of the disparate nature of the forces underlying these two anions.

There is a growing body of theoretical and experimental evidence demonstrating that these loosely bound, diffuse anions play a role in chemically and physically relevant phenomena. NVCB anions have been shown to: serve as gateways to valence anion states via low-energy electron
capture,\textsuperscript{1,4,5} play a role in the mobility of an electron solvated in liquid C\textsubscript{6}F\textsubscript{6}.\textsuperscript{6} create free-electron bands in 1D molecular C\textsubscript{60} chains and quantum wells in 2D C\textsubscript{60} clusters,\textsuperscript{7,8} form in noble gas clusters,\textsuperscript{9} and certain water clusters,\textsuperscript{10–12} which is related to the larger issue of the nature of the hydrated electron.\textsuperscript{13} Additionally, non-valence anions present fundamental questions as the molecules approach the nanoscale in size. At the nanoscale and larger, one is squarely within the realm of condensed matter physics where the diffuse anions of extended systems lying between the Fermi and vacuum energy levels are referred to as image potential states (IPSs). The name image potential state derives from the attractive self-induced image potential which binds the excess electron in a diffuse orbital. This long-range attractive potential arises from the charge distribution an excess electron induces in the solid, much like the dispersion-like correlation that binds an NVCB anion.

It has been suggested in the literature that NVCB anions and IPSs are related on the basis of the long-range electron correlation which dominates their binding.\textsuperscript{14–17} However, the connection between these diffuse anions, belonging to two different size regimes, has not been demonstrated outright. This works aims to do that by showing that the energetically low-lying NVCB anions of polycyclic aromatic hydrocarbon (PAH)s belonging to the chemical series C\textsubscript{6n}H\textsubscript{6n} n = 1, 2, 3, \ldots, and their corresponding carbon nanoflakes (C\textsubscript{6n}\textsuperscript{2}) evolve into the IPSs of graphene as the systems approach the nanoscale.

At the core of this work’s methodology is a so called cluster extrapolation procedure, which has been successfully used to estimate the surface binding energy of a single water molecule on an infinite graphene sheet.\textsuperscript{18–21} Figure 2 illustrates the cluster extrapolation procedure as a schematic. In essence, we will evaluate the electron binding energies EBEs, single particle electron orbitals and densities, as well as the dominant interactions underlying the NVCB anions of a series of increasingly large PAHs. The extrapolation terminates when one has demonstrated that there are large PAHs capable of supporting NVCB anions with EBEs and charge distributions characteristic of graphene’s IPSs.
Figure 2: Schematic illustration of the cluster extrapolation procedure used to demonstrate connection between the non-valence correlation-bound NVCB anions of polycyclic aromatic hydrocarbons (PAHs) and graphene’s image potential states (IPSs). The blue spheres represent an excess electron bound to the PAH molecules and an infinite graphene sheet. In the lower half of the image I represent the cluster extrapolation procedure as a continuous process of evaluating the properties, electron binding energies (EBEs), single particle orbitals $\phi(r)$, and single particle densities $\rho(r)$ of the NVCB anions of increasingly large PAHs until characteristics reminiscent of graphene’s IPSs are observed.

The size of the molecules and anionic states targeted in this work occupy a gray area lying between the domains of quantum chemistry and condensed matter physics. Consequentially, no routine theoretical method exists that can both accurately and efficiently describe the dispersion-like electron correlation underlying the non-valence anions of finite systems consisting of thousands of atoms. For NVCB anions a standard approach is to represent the molecular anion using an atom-
centered Gaussian basis augmented with diffuse functions in a wavefunction based method that incorporates higher order dynamic electronic correlation like electron affinity equation-of-motion Coupled Cluster Singles and Doubles (CCSD) (EA-EOM-CCSD)\textsuperscript{22} and EA-EOM-MP2.\textsuperscript{1,15,16,23–25} However, the canonical implementations of these approaches have steep scaling ($O(N^6)$) with system size ($N$) preventing application to molecules beyond tens of atoms. In the limit of an infinite sheet of graphene, a popular approach in the condensed matter physics community to simulating IPSs has included constructing a hybrid image potential and Density Functional Theory (DFT) potential in periodic boundary condition (PBC) calculations. Typically, this involves, “stitching together,” the exchange-correlation potential of a local DFT functional (e.g., local density approximation (LDA)) with the image potential at some predetermined cutoff distance, which delineates the short-range and long-range behavior of the hybrid potential respectively.\textsuperscript{26–28} However, by their very nature PBC calculations are meant to simulate an infinite system, like graphene, making this approach impractical to study the finite molecules of interest.

A major impasse is met without a computationally affordable and accurate method applicable to the broad scale of system sizes probed in this work. Fortunately, a promising alternative exists in the form of hybrid quantum mechanics/molecular mechanics model force field approaches. One-electron model Hamiltonians have been developed to simulate the NVCB anions of molecules and molecular clusters, ranging in size from tens to hundreds of atoms.\textsuperscript{12,14,29} This work documents progress in constructing a one-electron model Hamiltonian that can characterize the NVCB anions of PAHs and demonstrate their connection to the IPSs of graphene. In the ensuing chapters, I will provide the theoretical background (Chapter 2), present the first attempt made at developing a one-electron model Hamiltonian to characterize the lowest energy NVCB anion of small PAHs (Chapter 3), refinements made to the model potentials that allow for scaling up to tens of thousands of atoms (Chapters 4 and 5), and the application of the refined model to the low-lying NVCB states of large PAHs and carbon nanoflakes (Chapter 6).
2.0 Theory

This work aims to solve the time-independent electronic Schrödinger equation for a single excess electron bound to carbon-based systems consisting of tens to thousands of atoms. The Schrödinger equation can be represented as the eigenvalue problem (within the Born-Oppenheimer approximation),

\[ \hat{H}(\mathbf{r})\Psi(\mathbf{r}) = E(\mathbf{r})\Psi(\mathbf{r}) \]  

where \( \hat{H}(\mathbf{r}) \), \( \Psi(\mathbf{r}) \), and \( E(\mathbf{r}) \) represent the Hamiltonian operator, wavefunction, and energy of the excess electron respectively. To model the excess electron’s interaction with these molecules we employ a model Hamiltonian of the form,

\[ \hat{H}(\mathbf{r}) = \hat{T}(\mathbf{r}) + \hat{V}_{es}(\mathbf{r}) + \hat{V}_{pol}(\mathbf{r}) + \hat{V}_{rep}(\mathbf{r}) \]  

where \( \hat{T}(\mathbf{r}) \) is the kinetic energy operator for the excess electron and the operators \( \hat{V}_{es}(\mathbf{r}) \), \( \hat{V}_{pol}(\mathbf{r}) \), and \( \hat{V}_{rep}(\mathbf{r}) \) represent, respectively, the electrostatic, polarization, and repulsion potential that the excess electron (positioned at \( \mathbf{r} \)) experiences in the presence of the molecule. One will notice that equations 1 and 2 contain no explicit dependence on the molecule’s electrons or nuclei, as the molecule’s charge distribution and its interaction with the excess electron are represented approximately via the classical model potentials in equation 2. The operators in equation 2, \( V_{es}(\mathbf{r}) \), \( V_{pol}(\mathbf{r}) \), and \( V_{rep}(\mathbf{r}) \), provide the potential energy surface upon which the excess electron moves. The nature of the model potential and its parameterization are explained in detail in the subsequent chapters, but it is worth discussing the conceptual underpinnings that allow us to make this approximation and frame all of the work performed in developing the potential terms.

Unlike valence anions, the excess electron of NVCB anions binds weakly to the molecule with binding energies in the realm of tens to hundreds of meV. The resulting anion is spatially diffuse with the excess electron having a high probability of being tens of Ångstrom from the nuclei of the molecule. This implies that the electronic structure of the molecule is not significantly perturbed from its ground state geometry. Figure 3 shows a schematic which demonstrates this point.
Figure 3: Schematic illustration of the energy of a neutral molecule, a bound valence anion, and a bound non-valence anion as a function of change in molecular structure. The curves plot the energy of the molecule and molecular anions, horizontal lines indicate their ground state energies, and vertical lines the differences between the neutral and anion energies. Energy differences are labelled based on whether they represent adiabatic electron attachment (AEA) or vertical electron attachment (VEA). Energy differences between the neutral and valence anion are represented by the vertical red dotted lines. Energy differences between the neutral and non-valence anion are represented by the vertical solid blue lines.

In figure 3 the energy of a fictitious neutral molecule, the energy of its bound valence anion, and the energy of its bound non-valence anion are plot as a function of change in molecular structure. The energy differences between the neutral and anion when both are in their respective minimum energy geometries is the adiabatic electron affinity (AEA). The vertical electron affinity (VEA) represents the energy difference when both the neutral and anion are in the ground state geometry of the neutral molecule. One can see from the AEA that when the neutral molecule binds the excess
electron as a valence anion it causes a large shift in energy and molecular structure. Conversely, when the neutral molecule binds the excess electron as a non-valence anion there is a comparably smaller change in the ground state energy and molecular geometry.

The fact that the ground state configuration of the neutral molecule is not significantly altered when binding a non-valence anion indicates that the excess electron can be treated as a weak perturbation, more comparable to a non-covalent interaction than a valence anion. With this in mind, approximating the charge density belonging to the neutral molecule via classical model potentials becomes reasonable. Based on this reasoning, the potential terms in equation 2 can be parameterized on the ground state properties of the neutral molecule as well.

With this conceptual reasoning laid out, we can define what the potential terms in equation 2 represent more precisely. In this one-electron model, we clamp the excess electron at various positions \(r\) (similar in concept to the Born-Oppenheimer approximation) in space and evaluate its interaction with the neutral molecule’s charge distribution. The electrostatic potential \(V_{es}(r)\) models the interaction of the excess electron with unperturbed charge distribution of the molecule. The polarization potential \(V_{pol}(r)\) models the changes in the molecule’s charge density in response to the excess electron and the subsequent interaction between them. The repulsive potential \(V_{rep}(r)\) folds in, in an effective manner, the short-range interactions like exchange between excess and neutral molecule’s electrons and orthogonalization of the excess electron’s orbital to the energetically lower-lying occupied orbitals of the molecule. The following sections detail how one can extract properties from quantum mechanical calculations on neutral molecules and how they can be incorporated into the one-electron model.

2.1 Evaluation of Static Properties

In this work, we only concern ourselves with the time-independent response properties of a system. Time-independent, also referred to as static in this context, means that the system, its wavefunction, and concomitant properties do not evolve with the passage of time. The static properties of a system of electrons and nuclei, which we represent with wavefunction \(Ψ\), can be probed (experimentally and theoretically) by applying some small external perturbation \((V)\) and
measuring its response. Theoretically the properties of the system can be derived from its total energy \(E(V)\):
\[
E(V) = \frac{\langle \Psi | \hat{H}(V) | \Psi \rangle}{\langle \Psi | \Psi \rangle}
\]
with the perturbed Hamiltonian \(\hat{H}(V)\) being defined as:
\[
\hat{H}(V) = \hat{H}_0 + \lambda \hat{V}
\]
where \(\hat{H}_0\) is the ground state Hamiltonian of the system in the absence of external perturbation \(\hat{V}\), with complex scalar \(\lambda\).

If the external perturbation does not disturb the system appreciably from its ground state, the eigenfunctions of \(\hat{H}_0\) should provide a reasonable approximation to the true eigenfunctions of \(\hat{H}(V)\). Furthermore, a Maclaurin series expansion about the ground state energy \((E_0)\) which includes all perturbation components is valid.
\[
E(V) = \sum_{n=0}^{\infty} \frac{V^n}{n!} \frac{\partial^n E}{\partial V^n} = E_0 + \frac{V}{1!} \frac{\partial E}{\partial V} + \frac{V^2}{2!} \frac{\partial^2 E}{\partial V^2} + \frac{V^3}{3!} \frac{\partial^3 E}{\partial V^3} + \ldots
\]
The partial derivatives \(\partial^n E/\partial V^n\) above quantify the change in the system’s ground state energy in response to the external perturbation, meaning they represent the properties we are interested in extracting.

To demonstrate how we can extract the properties of a system from an observable we consider a relevant example, choosing the perturbation to be a point charge \(Q\) positioned at \(r = (r_x, r_y, r_z)\) relative to our system. In this example we are using \(Q\) as a probe and to determine the potential produced by a system’s charge density \(\rho(\mathbf{r}')\) centered at the origin. The potential produced by \(\rho(\mathbf{r}')\) at the position of the probe charge \(\mathbf{r}\) has the form \(V(\mathbf{r} - \mathbf{r}') = 1/\|\mathbf{r} - \mathbf{r}'\|\), where \(\|..\|\) denotes the Euclidean norm. Rather than solving for the potential exactly we can perform a Maclaurin expansion of the potential about some point within the charge density \(\mathbf{r}'\),
\[
V(\mathbf{r} - \mathbf{r}') = V_0(\mathbf{r}) + \frac{1}{1!} \mathbf{r}' : \frac{\partial V(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} + \frac{1}{2!} \mathbf{r}' \mathbf{r}' : \frac{\partial^2 V(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}' \partial \mathbf{r}'} + \ldots
\]
where \(V_0\) is the unperturbed ground state potential, \(\vdash\) represents a double dot product, and all other terms have been defined. Note that the potential is a function of the vector difference \(\mathbf{r} - \mathbf{r}'\), which defines the vector pointing from \(\rho(\mathbf{r}')\) to \(Q\). The derivatives of potential are with respect to \(\mathbf{r}'\) since we are expanding the potential about points within the charge density. To evaluate the total potential
produced by $\rho(r')$ at the point charge, the contribution of every particle making up the charge density must be summed,

$$V(r) = \int \rho(r') V(r - r') d^3r'$$

(7)

where it is implied that the integral is taken over all of real space ($\mathbb{R}^3$) with the finite volume element of our charge density in real space being $d^3r'$. This is equivalent to the following expression when we substitute in equation 6, distribute terms, and simplify.

$$V(r) = \int [\rho(r') d^3r'] V_0 (r) + \int [\rho(r') \cdot r' d^3r'] \cdot \frac{\partial V(r - r')}{\partial r'} + \frac{1}{2} \int [\rho(r') \cdot r' r' d^3r'] \cdot \frac{\partial^2 V(r - r')}{\partial r' \partial r'} + \ldots$$

(8)

One may recognize the above integrals as the charge ($q = \int \rho(r') d^3r'$), dipole vector ($\mu = \int \rho(r') \cdot r' d^3r'$), and second rank quadrupole tensor ($\tilde{\Theta} = \int \rho(r') : r' r' d^3r'$) of the charge density $\rho(r')$. We can evaluate the derivatives of the Coulomb potential $V(r - r') = 1/|r - r'|$ revealing the fundamental electrostatic identities,

$$V_0 (r) = \frac{1}{r}$$

(9)

$$F(r) = -\frac{\partial V(r - r')}{\partial r'} = \frac{r}{r^3}$$

(10)

$$\ddot{G}(r) = -\frac{\partial^2 V(r - r')}{\partial r' \partial r'} = \frac{rr}{r^5}$$

(11)

where $r = \|r\|$ meaning $r$ is the Euclidean norm of the vector $r$. We see that the first derivative is equivalent to the electric field vector ($F$) and the second derivative, the electric field gradient ($\ddot{G}$). Thus, we have the final expression,

$$V(r) = qV_0 (r) - \mu \cdot F(r) - \frac{1}{2} (\tilde{\Theta} : \ddot{G}(r)) + \ldots$$

(12)

Taking derivatives of equation 12 with respect to each component of the electrostatic potential expansion we observe the following relationships,

$$\frac{\partial V(r)}{\partial V_0 (r)} = q$$

(13)

$$\frac{\partial V(r)}{\partial F(r)} = -\mu$$

(14)

$$\frac{\partial V(r)}{\partial \ddot{G}(r)} = -\frac{1}{2} \tilde{\Theta}$$

(15)
One can evaluate the interaction energy of the point charge with the charge density by simply multiplying its value into equation 12.

\[ E(r) = Q \left[ qV_0(r) - \mu \cdot F(r) - \frac{1}{2} (\vec{\Theta} : \vec{G}(r)) + \ldots \right] \]  

(16)

Taking the point charge to be unity \((Q = 1)\), we evaluate the derivatives of equation 16 with respect to each component of the electrostatic potential expansion we observe the following relationships,

\[ \frac{\partial E(r)}{\partial V_0(r)} = q \]  

(17)

\[ \frac{\partial E(r)}{\partial F(r)} = -\mu \]  

(18)

\[ \frac{\partial E(r)}{\partial \vec{G}(r)} = \frac{\partial^2 E(r)}{\partial F(r) \partial F(r)} = -\frac{1}{2} \vec{\Theta} \]  

(19)

This gives us the direct relationships between observables like electrostatic potential and energy with properties. In essence, this is a classical analog of the Hellmann-Feynman theorem which shows that any observable property of a system is equivalent to the derivatives of its expectation value with respect to a perturbation, or \( \partial \langle \Psi | \hat{H}(V) | \Psi \rangle / \partial V \).

The multipoles of \( \rho(r') \) extracted in equation 12 contain the potential contributions of the static charge density as well as changes in the charge density in response to the external charge. For instance, if we are interested in the multipole contributions to \( \mu \) that are induced by the external probe charge we can perform yet another Maclaurin expansion, this time about \( \mu \) with respect to the electric field, \( F(r) \),

\[ \mu(F(r)) = \mu_0 + F(r) \cdot \frac{\partial \mu}{\partial F(r)} + \frac{1}{2} F(r) F(r) : \frac{\partial^2 \mu}{\partial F(r) \partial F(r)} + \ldots \]  

(20)

where \( \mu_0 \) is the static dipole moment of the system and all higher order terms represent induced multipole corrections to the total dipole moment. If we substitute our energy-dipole relation from equation 18 into equation 20 we obtain the following expression,

\[ \mu(F(r)) = \frac{\partial E_0}{\partial F(r)} - F(r) \cdot \frac{\partial^2 E}{\partial F(r) \partial F(r)} - \frac{1}{2} F(r) F(r) : \frac{\partial^3 E}{\partial F(r) \partial F(r) \partial F(r)} + \ldots \]  

(21)
where the first term relates the ground state energy to permanent dipole with all higher order terms being induced energetic corrections to it. One may recognize these corrections as the dipole polarizability and first hyperpolarizability,

$$\frac{\partial \mu}{\partial F(r)} = -\frac{\partial^2 E}{\partial F(r) \partial F(r)} = \tilde{\alpha}$$

$$\frac{\partial^2 \mu}{\partial F(r) \partial F(r)} = -\frac{\partial^3 E}{\partial F(r) \partial F(r) \partial F(r)} = \frac{1}{2} \beta \ldots$$

which are represented by the second rank tensor \(\tilde{\alpha}\) and third rank tensor \(\beta\) respectively. Thus, the dipole polarizability and first hyperpolarizability are related to the energy of the system through the electric field derivatives and equation 21 becomes the final expression for the induced dipole.

$$\mu(F) = \mu_0 + F \cdot \tilde{\alpha} + \frac{1}{2} FF : \beta + \ldots$$

One can perform the same expansion to determine the leading order corrections to \(\tilde{\Theta}\) and all higher order terms in equation 12. With the relationships between properties and energy demonstrated, we shall turn our attention to the methods employed in this work.

### 2.2 Electrostatic Multipoles

In section 2.1 it was shown that one can extract the properties of a system’s charge density by measuring its electrostatic potential and expressing that as a series expansion. The resulting expression, equation 16, contains both permanent (non-perturbation dependent) and inducible (perturbation dependent) multipole moments that contribute to the observed potential. Here we concern ourselves with extracting only the permanent multipole moments for use in a model force field. In equation 16 it was presumed that the cumulative potential and consequentially molecular multipoles of the system were computed or measured in a single center multipole expansion (SCME) at the center of mass. Molecular multipoles are not the best method of representing the static charge density in simulations, rather it is standard in modern force fields to use a distributed multipole expansion (DME), where every atom in a molecule is assigned its own set of multipoles \((q, \mu, \ldots)\).
The main reasons for doing so are: capturing local anisotropy of a system’s charge distribution and the validity of the multipole expansion near the molecule’s charge distribution.

The first point is relatively self-explanatory, distributing the description of electrostatics over the atoms of the system will provide a detailed picture of the spatial dependence of a molecule’s electrostatic potential. Consider a diatomic molecule with a dipole where one can use a SCME via a single molecular dipole at center of mass. However, we know that this dipole is the result of an unequal sharing of electrons between the bound atoms. If one uses atomic charges in a DME that reproduce the total molecular dipole, we recover information about the local atomic charge distributions which can align with or challenge our chemical intuition derived from concepts like electronegativity. Furthermore, the inclusion of higher order terms like atomic dipoles can provide a finer description of local charge densities, capturing the contribution of atomic lone pairs to the total electrostatic potential.

The second point is more easily illustrated with a specific example. We scan along the axis normal to the molecular plane of water (x-axis in this example), measuring the electrostatic potential produced by the charge density of a PBE0/aug-cc-pVTZ calculation. From this same density we extract the molecular (SCME) and atomic multipole moments (DME) and calculate the error in their electrostatic potential relative to the reference DFT potential. Figure 4 plots the magnitude of the error of the two model electrostatic potentials relative to the reference DFT potential.
Figure 4: Magnitude of error in electrostatic potential produced by a single center multipole expansion (SCME) and distributed multipole expansion (DME) relative to a PBE0/aug-cc-pVTZ calculation.\textsuperscript{33–38} Subplot (a) shows the error in the electrostatic potential of H$_2$O as described by the atomic multipoles (blue curve) and molecular moments (black curve) extracted from PBE0/aug-cc-pVTZ density using Gaussian distributed multipole analysis (GDMA).\textsuperscript{39} Subplot (b) is a schematic showing the orientation of Cartesian axes at the water molecule’s center of mass, the placement of the molecular multipoles ($\mu_{\text{H}_2\text{O}}$, $\Theta_{\text{H}_2\text{O}}$, \ldots) at the center of mass in the SCME, and placement of atomic multipoles (e.g. $\mu_{\text{O}}$, $\Theta_{\text{O}}$, \ldots for oxygen) at their respective atomic centers in the DME. Both the DME and SCME terminate at the sixth moment in the expansion (the 32-pole). The electrostatic potential scan is taken along the $x$-axis, which is normal to the molecular plane, and the resulting error in model potentials is plotted with respect to the distance from water’s center of mass along the $x$-axis.

Comparing the error in the SCME and DME electrostatic potentials one can see that they are essentially the same at long-range, slowly decaying to zero. However, as one gets closer to the molecule the error in the SCME grows more rapidly than that of the DME. As the point charge
approaches the charge distribution of water, charge penetration (an electrostatic interaction arising from overlap in charge densities) grows in importance, but is not described by molecular or atomic electrostatic multipoles. Since the charge penetration error is common to both methods it does not help clarify, whether the SCME or DME is more accurate. The van der Waals radius of a molecule can provide a rough estimate for when charge penetration effects become appreciable. Many force fields studying solvated proteins will treat water as a spherical probe with a van der Waals radius between 1.4 and 1.8 Å. The point charge in this example calculation is well outside the region of van der Waals contact of water. Additionally, Bizzarro, Egan, and Paesani performed model calculations on water-halide pairs with and without short-range electrostatic effects (including charge penetration) and by comparing to DFT results it was demonstrated that for the smallest halide anion, F-, short-range electrostatic effects are not severe around 3 Å. Given that we use a point charge in this example calculation, the above results suggest that the error in the model SCME and DME electrostatic potentials should not be influenced by charge penetration for the distances we consider (3 to 6 Å). With that in mind, we see that the DME description of electrostatics incurs less error than that of an SCME at separations relevant to non-covalent interactions. Although the error of both models is small in this point charge and water system, it can become appreciable when one treats large, more complex systems.

Now that we have motivated the use of atomic multipoles in a model force field, we turn our attention to how one calculates them. An inherent difficulty of atoms in molecules and their properties is that they are patently non-observable, meaning they can not be measured experimentally unlike their molecular counterparts. This means that one can not state outright that any set of atomic multipoles constitute the, "correct," representation of a static charge distribution. As one might imagine, this has led to a proliferation of methods all attempting to solve the same problem. A discussion of all the DME methods is not within the scope of this work, but the following paper by Cho et al. compares DME schemes for calculating partial atomic charges, many of which can be extended to obtain higher order atomic multipoles. It is worth commenting that the major arguments for or against any distributed multipole scheme boil down to the following list.

- Accuracy: Reproduction of theoretical or experimental observable benchmarks like accurate electrostatic potentials.
- Generality: Does the method perform well for a variety of systems?
• Efficiency: Is the method fast and does it use a reasonable amount of computational resources.
• Uniqueness: Is there a way to verify that the final set of multipoles represent a unique solution within the framework of the applied theory?
• Simplicity: Are the multipoles produced easy to use in applications?

The above criteria represent a framework one may use to assess the value and validity of one method over another. The first three points are self-explanatory and do not require any further explanation. The question of uniqueness is usually answered with mathematical arguments and it is important to prove for methodological development. However, it falls outside the scope of this work. For those interested, a review by Farnaz et al. on the class of information-theoretic DME methods does the subject justice.\(^{43}\) The last point, simplicity, is a practical consideration worth discussing further and it is one we explore in chapter 4.

As a closing topic, I will briefly comment on how one defines an atom within a molecule and allocates multipole moments. Generally speaking, the popular methods of partitioning a molecule into atomic domains are based on the properties (e.g. electrostatic potential), Hilbert space (i.e. orbital basis), or electron density of the system. Property-based DME methods\(^ {44–47}\) will evaluate the molecular electrostatic potential from a quantum mechanical calculation at a series of grid points in real space and fit multipoles centered at atomic nuclei to reproduce the reference potential. These methods differ in the real space grids they use and the constraints they apply to their fitting procedures, but at their core they are fundamentally the same. Hilbert (basis) space DME methods allocate atomic domains by decomposing the one-electron charge density into the atomic orbital basis set functions.\(^ {48–50}\) These approaches may recast the basis set in some manner, using say symmetric orthogonalization in the case of Löwdin,\(^ {49}\) but they start with the atomic orbital basis as a means for partitioning the molecular density into atomic domains. The last set of DME methods work directly with the molecular density in real space to allocate molecular charge density to atoms.\(^ {51–60}\)

### 2.2.1 Gaussian Distributed Multipole Analysis

In addition to the approaches discussed in section 2.2 there are methods that work in a mixed basis-real space approach using information from the orbital basis and molecular density. We use
atomic multipoles derived from mixed basis-real space DME methods in our one-electron model Hamiltonian, thus the manner in which they allocate atomic domains and multipoles warrants further discussion. Gaussian distributed multipole analysis (GDMA)

is a popular mixed basis-real space approach where the allocation of atomic domains is handled one of two ways:

- Using the one-electron density matrix coefficients and atomic orbital basis functions.
- Using atom centered real space grids similar to those employed in DFT.

To demonstrate why using a mixed basis-real space approach becomes necessary in this method we must lay out the basic theory of GDMA. If one expands the single particle molecular density in its atomic basis functions they obtain the following expression,

\[ \rho(r) = \sum_{ab} P_{ab} \chi_a(r-a) \chi_b(r-b) \]  \hspace{1cm} (25)

where \( \chi_a(r-a) \) and \( \chi_b(r-b) \) are basis functions centered at \( r_a \) and \( r_b \) respectively and \( P_{ab} \) are the corresponding density matrix coefficients. If one is working with Gaussian basis functions, they can express the product of \( \chi_a \) and \( \chi_b \) as such,

\[ \chi_a(r-a) \chi_b(r-b) = e^{-\alpha(r-a)^2} \times e^{-\beta(r-b)^2} \]  \hspace{1cm} (26)

where we have expressed the atomic orbitals in terms of their exponential and polynomial (\( f_{l\alpha m\alpha} \) and \( f_{l\beta m\beta} \)) components with angular momenta \( l \) and magnetic quantum number \( m \). It is well known that the product of two Gaussian functions centered at \( a \) and \( b \) produces a third Gaussian centered on point \( S \), which lies between the two Gaussians. Applying this to equation 26 we obtain,

\[ \chi_a(r-r_a) \chi_b(r-r_b) = e^{-\frac{\alpha\beta(r_a-r_b)^2}{\alpha+\beta}} \times \left( f_{l\alpha m\alpha}(r-r_a) \times f_{l\beta m\beta}(r-r_b) \right) \]  \hspace{1cm} (27)

where all terms have been defined. For every pair of Gaussians in equation 25, we now have an origin \( S \) about which we can perform a multipole expansion to obtain electrostatic moments. The multipoles are obtained by integration over the overlap charge density and regular solid harmonic \( R_{kq}(r-S) \) centered at origin \( S \),

\[ Q_{kq}(r_S) = -\int R_{kq}(r-r_S) P_{ab} \chi_a(r-r_a) \chi_b(r-r_b) d^3r, \]  \hspace{1cm} (28)
where one can substitute the Gaussian product of equation 27 into equation 28 placing the integrand in terms of functions centered on \( S \). When a point of overlap \( S \) does not coincide with the position of a nucleus, the resulting multipole moments are moved to the nearest atomic nucleus.

If one employs spatially diffuse atomic orbitals they may find that the total charge distribution changes very little between basis sets, but the atomic multipoles vary considerably. This issue is common to many of the Hilbert space approaches (e.g. Mulliken\cite{48} and Löwdin\cite{49}), which inherently depend upon the nature of the basis set employed. To remedy this issue, GDMA switches to real space quadrature for the diffuse functions. In essence, the program constructs a spherical grid of points in real space for every atom and evaluates the integrand of equation 28 using Becke’s quadrature algorithm.\footnote{61} The weights of the quadrature scheme allow atomic grids to interpenetrate smoothly, improving the handling of Gaussian products associated with diffuse functions spanning multiple nuclei. Switching to a real space representation for diffuse atomic orbitals removes much of the basis set dependence associated with the partitioning scheme outlined above.

### 2.2.2 Basis Space-Iterated Stockholder Atoms

The second mixed basis-real space approach we employ to obtain model electrostatic multipoles is basis space-iterated stockholder atoms (BS-ISA).\footnote{64} This DME method is based upon the iterated stockholder atoms\cite{58,59} approach whose core equations are captured by two expressions,

\[
\rho_A(r) = \left( \frac{\rho_A^0(r)}{\sum_B \rho_B^0(r)} \right) \rho_{\text{mol}}(r) \tag{29}
\]

\[
\rho_A^0(r) = \langle \rho_A(r) \rangle_{\text{sph}} \tag{30}
\]

where the first expression comes from Hirshfeld\cite{54} and equates the density of atom \( A \), \( \rho_A \), to the molecular density \( \rho_{\text{mol}} \) weighted by the ratio of atom \( A \)’s promolecular (free atom) density, \( \rho_A^0 \), and the sum of all proatom densities \( \rho_B^0 \) within the molecule. The ambiguous (non-observable) quantity in equation 29 are the proatomic densities and various extensions of Hirshfeld’s work have been formulated each providing its own definition of this quantity.\footnote{52,55–57,60} In iterated stockholder atoms the proatomic densities are defined as the spherical average of the atomic densities (equation 30). One can see that equations 29 and 30 depend on one another, meaning that one must make an initial guess for the \( \rho^0 \) and then iterate the equations until the atomic densities converge. As one iterates
these equations the initial guesses for the proatoms relax, picking up bonding information within their chemical environments.

The above equations work in real space with grids designated for the molecular and proatomic densities. The conceptual simplicity of the approach is appealing, but the speed with which the iterations converge is sensitive to the initial guess for the proatomic densities. To address this practical issue of efficiency BS-ISA expands all the quantities in equations 29 and 30 in auxiliary basis functions like so,

\[ \rho_{mol}(r) \sim \tilde{\rho}_{mol}(r) = \sum_k c_k \chi_k(r) \]  
\[ \rho_A(r) \sim \tilde{\rho}_A(r) = \sum_k c_k^A \chi_k^A(r) \]  
\[ \rho_0^A(r) = \sum_{k \in \mathbb{S}} c_k^A \chi_k^A(r) \]

where \( \chi_k(r) \) and \( \chi_k^A(r) \) are Gaussian orbitals for the molecular and atomic densities and \( c_k \) and \( c_k^A \) their respective fitting coefficients. Note that the proatomic densities are expanded in only the s-functions \( (k \in \mathbb{s}) \) of the basis \( k \) used to fit the atomic densities. Standard density fitting techniques are employed only once at the beginning of the calculation to expand the molecular density in its auxiliary basis set.65–67 Next, one solves equations 29 and 30 by minimizing the atomic Stockholder functional \( \Delta_A \),

\[
\Delta_A = \int d^3r \int d^3r' \left[ \tilde{\rho}_A(r - r_A) - \left( \frac{\rho_0^A(r - r_A)}{\sum_B \rho_0^B(r - r_B)} \right) \tilde{\rho}_{mol}(r) \right] \times \delta(r - r') \\
\times \left[ \tilde{\rho}_A(r' - r_A) - \left( \frac{\rho_0^A(r' - r_A)}{\sum_B \rho_0^B(r' - r_B)} \right) \tilde{\rho}_{mol}(r') \right]
\]

where one is evaluating the overlap norm \( \langle \delta(r - r') \rangle \) by performing a six dimensional integral in real space. At each iteration, BS-ISA evaluates equation 34 for every atom independently and simultaneously, enabling parallelization of the routine. Once an iteration ends, the proatomic densities are updated via equation 30 and one evaluates 29. Equation 34 is evaluated until the left and right hand sides of equation 29 agree to a predetermined threshold, at which point the atomic multipoles are extracted using the following equation,

\[
Q_{kq}^A(r_A) = \int R_{kq}(r - r_A) \left( \frac{\rho_0^A(r - r_A)}{\sum_B \rho_0^B(r - r_B)} \right) \rho_{mol}(r) d^3r
\]
where all terms have already been defined. As a final note, equation 35 is evaluated using real-space grids rather than the auxiliary basis functions, as the finite basis sets used to fit the atomic, pro-atomic, and molecular densities are incomplete. Thus, using real space grids in this final step tends to yield more accurate results.

2.3 Quantum Mechanical Polarizabilities

We established in section 2.1 that the first two corrections to a dipole in an external electric field and its energy are the terms representing the polarization response of a system to the external field. Now, we turn our attention to how the leading order correction $\alpha$ is calculated in the ensuing chapters. For many quantum mechanical methods the analytical expressions for the derivative in equation 22 are known. However, analytical derivatives are not always known for more sophisticated methods and for those employing a single determinant to represent a wavefunction, like HF and DFT, one typically needs to solve the coupled perturbed SCF (CPSCF) equations. The typical implementations of CPSCF work with canonical molecular orbitals and scale as $O(N^5)$ with system size making it resource intensive for large systems. An alternative to this is performing numerical differentiation to evaluate the derivatives in equation 22, which we employ exclusively for obtaining reference polarizabilities in this work. To illustrate how these calculations work, we consider a simple fictitious example where we have a neutral system without a permanent dipole moment interacting with a uniform electric field. The polarizability $\alpha$ and first hyperpolarizability $\beta$ enter the dipole and energy expressions like so,

\[ \mu^{\text{ind}}(F) \approx \alpha \cdot F + \frac{1}{2} \beta : FF \] 
\[ E(F) \approx E_0 - \frac{1}{2} \alpha : FF - \frac{1}{6} \beta : FFF \]

where we indicate that we are solving for the induced dipole, $\mu^{\text{ind}}$, only as $\mu_0 = 0$ and all other terms and operations have been defined previously. To simplify further, let us presume that we are interested in calculating only the zz-component of the dipole polarizability tensor of the system.
To achieve this we apply a uniform electric field in the z-direction, along which lies our fictional system of interest. The above equations then reduce to,

\[
\mu_{\text{ind}}^z (F_z) \approx \alpha_{zz} F_z + \frac{1}{2} \beta_{zzz} F_z^2
\]

\[
E(F_z) \approx E_0 - \frac{1}{2} \alpha_{zz} F_z^2 - \frac{1}{6} \beta_{zzz} F_z^3
\]

where \( F_z, \alpha_{zz}, \) and \( \beta_{zzz} \) are the z-component of the external electric field, the zz-component of the dipole polarizability tensor, and zzz-component of the first hyperpolarizability tensor respectively. For this fictitious example we choose \( \alpha_{zz} = \beta_{zzz} = 2 \text{ a.u.}, E_0 = -5 \text{ a.u.}, \) and \( \mu_0 = 0 \text{ a.u.} \) By applying fields of different strengths one observes the following energy-field and dipole-field relationships in figures 5a and 5b.
Figure 5: Energy $E(F_z)$ and $z$-component of the dipole $\mu_z(F_z)$ of a charge neutral fictional system in a uniform electric field along the $z$-axis, $F_z$. We consider the first two corrections to the dipole and energy expansion, the dipole polarizability ($\alpha$) and first hyperpolarizability ($\beta$). Since the external electric field has one non-zero component along $z$ and the fictional system lies along this axis all induced multipole components vanish except those aligned with the field, $\alpha_{zz}$ and $\beta_{zzz}$, which are both chosen to equal 2 a.u. Figure insets show the value of the functions near the ground state unperturbed dipole $\mu_0 = 0$ and energy $E_0 = -5$ a.u. Red points and dashed line show the dipole and energy values and approximations to $\mu(F_z)$ and $E(F_z)$ when the contribution of $\beta_{zzz}$ is neglected near the ground state. Red points are annotated to indicate the value of the function at the positive or negative ($\pm \Delta F_z$) field step in a 3-point finite central difference approximation to the derivatives $d\mu(F_z)/dF_z$ and $d^2E(F_z)/dF_z^2$.

As can be seen in figure 5a the dipole field dependence is roughly linear when the applied field is $-0.2 \leq F_z \leq 0.2$. Outside this region one starts to observe quadratic field dependence due to the growing dominance of second term in equation 38. The influence of the quadratic field term becomes appreciable at stronger field strengths. This can be problematic when one considers how we will be extracting the multipole moments. We know from the identity in equation 22, that we
can extract $\alpha_{zz}$ by evaluating the derivative of the induced dipole with respect to the field. We can approximate the derivative of the induced dipole with respect to field strength about the unperturbed dipole, $\mu(F_z = 0) \rightarrow \mu_0$, using the 3-point central finite difference formula,

$$
\frac{d\mu(F_z)}{dF_z} \approx \frac{\mu(\Delta F_z) - \mu(-\Delta F_z)}{2\Delta F_z} \approx \alpha_{zz} + \beta_{zzz}F_z \varepsilon(F_z)
$$

(40)

where all terms have been defined except $\Delta F_z$, which is the field step in the finite difference scheme. In this particular example $\Delta F_z = \pm 0.001$ and since we performing an expansion about $F_z = 0$ the set of grid points we use in equation 40 are $F_z = -0.001$, 0, and 0.001. Given that $\mu(F_z)$ is linear at these field strengths, as can be seen in the figure inset, we can safely ignore the contribution of $\beta_{zzz}$ treating it as an error on the order of $F_z$ in our derivative.

Alternatively, one can approximate the second derivative of the energy with respect to the applied field using the following 3-point central finite difference formula about the unperturbed energy, $E(F_z = 0) \rightarrow E_0$,

$$
\frac{d^2E(F_z)}{dF_z^2} \approx -\left[\frac{dE(\Delta F_z)}{dF_z} + \frac{dE(-\Delta F_z)}{dF_z}\right] = -\left[\frac{E(2\Delta F_z)-E(\Delta F_z-\Delta F_z)}{2\Delta F_z} - \frac{E(\Delta F_z+\Delta F_z)-E(-2\Delta F_z)}{2\Delta F_z}\right]
$$

(41)

$$
= \frac{2E_0 - E(2\Delta F_z) - E(-2\Delta F_z)}{4\Delta F_z^2} \approx -\alpha_{zz} + \beta_{zzz}F_z \varepsilon(F_z)
$$

where on the first line we have equated the second derivative of $E(F_z)$ to a 3-point central difference of the first derivative of $E(\Delta F_z)$, in which we substitute the negative of the final expression from equation 40 in terms of energy. We negate the expression because the second derivative of energy is opposite in sign to the first derivative of the induced dipole (see equation 22). On the second line, we simplify the numerical derivative and equate it to the r.h.s. of equation 39.

It can be seen in figure 5b that the energy is roughly quadratic with respect to the external field in the domain $-0.3 \leq F_z \leq 0.3$, but at larger field strengths the cubic dependence of the first hyperpolarizability becomes appreciable. We see in the inset of figure 4b that by probing near the ground state energy with a field step of $2 \times \Delta F_z = \pm 2(0.001) = \pm 0.002$, one can safely ignore the influence of the first hyperpolarizability, treating it as a small error in the calculation on the order of $F_z$.

With this simple example we have demonstrated how one can obtain the dipole polarizability from a quantum mechanical calculation of the perturbed energy or induced dipole in a uniform
electric field. The fictitious data used is admittedly somewhat idealized as in real quantum mechanical calculations one must consider the influence of higher order polarizabilities, but so long as the electric field strength is chosen carefully contamination should be a non-issue. On the other hand, one must not make the field strength too small as there is inherent error in both the applied quantum mechanical method, as well as the finite difference approximation. The former issue can be addressed by converging the quantum mechanical calculation to a tighter tolerance in energy or density, but the latter is more tricky. Both equation 40 and 41 are accurate to $O(F_z^2)$ in the applied electric field, so if the change in $E(F_z)$ or $\mu(F_z)$ is too small for a given value of $F_z$ (e.g. 0.001) the calculated value of $\alpha$ may land within in the noise of the finite difference approximation (e.g. $1E^{-6}$). Thus, one must experiment with the values of $F_z$ used and the finite difference approximation employed. Generally speaking, a mixed analytical-numerical procedure to differentiation is more tolerant to the aforementioned issues, so we opt for a first derivative of the induced dipole from a quantum mechanical method (e.g. DFT and MP2) in all our calculations.

### 2.4 Model Polarizabilities

Now that we understand how reference molecular polarizabilities are calculated, we will briefly review the details of how these values are used to parameterize our model. I will not re-litigate all the details of how parameters were determined exactly. For those interested, details can be found in chapter 3 regarding the parameter tuning for small PAHs and chapter 5 discusses the parameter tuning for reproducing the image potential of an infinite conducting sheet. Instead, this section will describe how one obtains molecular dipole polarizabilities from our model, which can be referenced against and tuned to reproduce quantum mechanical results.

Our model employs both atomic inducible charges $q$ and dipoles $p$, which couple to the external electric potential ($V_i = Q/R_{ie}$) and field ($F_i = [-Q \cdot R_{ie}]/R_{ie}^3$) of the excess electron ($Q$) respectively, where $R_{ie}$ is the vector pointing from the electron to atom $i$ and $R_{ie}$ its magnitude. The model is an extension of that by Mayer and Åstrand, where fluctuating atomic charges are coupled with atomic inducible dipoles, allowing for screened inducible charge-charge, charge-dipole/dipole-charge, and dipole-dipole interactions within a molecule. The approach of combining inducible
charges and dipoles is not novel (for instance see\textsuperscript{73,74}) and as was discussed in section 2.3 even more accurate approximations to the polarization energy can be obtained by including higher order atomic polarizabilities. With that being said, the polarization energy in our model is calculated with the following expression:

\[ E_{pol} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} q_i T_{q-q}^{i,j} q_j - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} p_i \cdot T_{p-p}^{i,j} p_j - \sum_{i=1}^{N} \sum_{j=1}^{N} p_i \cdot T_{p-q}^{i,j} q_j + \sum_{i=1}^{N} q_i V_i - \sum_{i=1}^{N} p_i \cdot F_i \] (42)

where \( q_i \) refers to the induced charge and \( p_i \) the induced dipole vector of atom \( i \) and \( N \) is the number of atomic sites in the molecule. The entries \( T_{q-q}, T_{p-p}, T_{q-p}, \) and \( T_{p-q} \) are tensor matrices containing the damped charge-charge, dipole-dipole, charge-dipole, and dipole-charge interaction equations respectively. These functions include damping terms derived with the assumption that the atomic charge distributions are well described by Gaussian functions. These damping terms are crucial to avoid the so called, "polarization catastrophe," which refers to the divergence in polarization energy that occurs as inter-atomic distances shrink.\textsuperscript{75}

There is an additional constraint applied to the induced charges,

\[ f = E_{pol} + \Lambda \left( \sum_{i=1}^{N} q_i - q_{mol} \right) \] (43)

which ensures that the sum of induced charges equals the total induced molecular charge \( q_{mol} \) via a global coupling through the Lagrange multiplier \( \Lambda \). Solving the system of equations in 43 amounts to finding the minimum of the derivative \( df/d\nu \) where \( \nu \) represents \( q_i, p_i, \) and \( \Lambda \). One can recast this system of equations into the following form using linear algebra,

\[
\begin{pmatrix}
T_{q-q} & -T_{q-p} & 1 \\
-T_{p-q} & -T_{p-p} & 0 \\
1 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
q \\
p \\
\Lambda
\end{pmatrix}
= 
\begin{pmatrix}
-V \\
F \\
q_{mol}
\end{pmatrix}
\] (44)

where the overall dimension of the left hand matrix is \( 4N + 1 \times 4N + 1 \), \( q = (q_1, \ldots, q_i, \ldots, q_N) \) is of length \( N \), and \( p = (p_{1x}, p_{1y}, p_{1z}, \ldots, p_{Nx}, p_{Ny}, p_{Nz}) \) is of length \( 3N \). The vectors \( V = (V_1, \ldots, V_i, \ldots, V_N) \) \( F = (F_{1x}, F_{1y}, F_{1z}, \ldots, F_{Nx}, F_{Ny}, F_{Nz}) \) contain respectively, the value of the potential and electric field of the electron at every atom. The entries \( 1 \) and \( 0 \), represent a vector of ones of length \( N \) and of zeros of length \( 3N \), respectively. The vector of ones is included to ensure that the overall charge of the system is constrained to \( q_{mol} \).
The dot product of the inverse matrix with both sides of the equality yields the vector of induced atomic charges and dipoles.

\[
\begin{pmatrix}
q_p \\
\Lambda
\end{pmatrix} = \begin{pmatrix}
T_{q-q} & -T_{q-p} & 1 \\
-T_{p-q} & -T_{p-p} & 0 \\
1 & 0 & 0
\end{pmatrix}^{-1} \begin{pmatrix}
-V \\
F
\end{pmatrix}
\]

To obtain the polarization energy one merely needs to take another dot product.

\[
E_{pol} = \frac{1}{2} \begin{pmatrix}
-V \\
F
\end{pmatrix} \cdot \begin{pmatrix}
q_p \\
\Lambda
\end{pmatrix} = \frac{1}{2} \begin{pmatrix}
-V \\
F
\end{pmatrix} \cdot \begin{pmatrix}
T_{q-q} & -T_{q-p} & 1 \\
-T_{p-q} & -T_{p-p} & 0 \\
1 & 0 & 0
\end{pmatrix}^{-1} \begin{pmatrix}
-V \\
F
\end{pmatrix}
\]

where the factor of 1/2 is applied to remove any doubly counted contributions. The sum of these induced moments yields the molecular induced dipole,

\[
\mu_{ind} = \sum_{i=1}^{N} (q_i \mathbf{r}_i + p_i)
\]

where \( \mathbf{r}_i = (x_i, y_i, z_i) \) is the coordinate of atom \( i \). Summing over the tensor blocks of the inverted matrix on the right hand side of equation 45, which we will notate with the shorthand \( \alpha_{pol} \), one can recover the 3 × 3 molecular polarizability tensor.

\[
\tilde{\alpha} = \sum_{j=1}^{N} \sum_{i=1}^{N} \left( \alpha_{pol}^{q_i q_j} \mathbf{r}_j \otimes \mathbf{r}_i - 2 \alpha_{pol}^{q_i p_j} \otimes \mathbf{r}_i + \alpha_{pol}^{p_i p_j} \right)
\]

With these connections drawn, one can see the direct relationship between the classical equations for an induced dipole in a uniform field (equations 36 and 37) and the inducible atomic multipole model (equations 45 and 46). We are solving for the quantities in these expressions,

\[
\mu_{ind}(\mathbf{F}) = \tilde{\alpha} \cdot \mathbf{F}
\]

\[
E_{pol}(\mathbf{F}) = \frac{1}{2} \tilde{\alpha} : \mathbf{F} \mathbf{F}
\]

where \( E_0 \) is absent because we are calculating the \( E_{pol} \) as a component of the electron binding energy of an anion, not the total energy of the molecular anion. The molecular induced dipole, static dipole polarizability, and polarization energy are all observable quantities that model parameters can be tuned to reproduce. As was discussed in section 2.3, one can extract the molecular dipole...
polarizability from quantum mechanical calculations analytically or using finite differentiation. As one will see in later chapters, we use the molecular polarizabilities and polarization potentials from DFT and MP2 calculations to tune our model parameters.

On a closing note, it is worth couching the above model in the context of existing methods in the literature. Although we have been discussing our polarization model, the above equations are generic. Without specifying the nature of the screening between inducible atomic moments in $T_{q-q}$ and $T_{p-p}$, one can recover a variety of polarization models from the above equations. A fluctuating charge model is obtained if the inducible dipoles are dropped from $\alpha_{pol}$. The fluctuating charge method has been used in both its original\(^{71,72}\) and revised\(^{76-82}\) forms in many force fields. Inducible atomic dipole models are a very popular alternative,\(^{30,83-89}\) as they are inherently anisotropic including the movement of charge density outside the plane of atoms. One can include, "dummy atoms," in fluctuating charge models to capture this same behavior, but a reasonable bonding distance must be selected for every unique dummy atom which is not known a priori. The inherent locality of inducible atomic dipoles can not accurately describe fluctuations in charge density over long distances, which is the dominant source of polarization in conjugated systems exhibiting heavy electron delocalization. Fluctuating charge models capture this charge delocalization quite readily and we demonstrate the importance of this in chapters 3 and 5.

Beyond the functional form of screening of inducible moments these models can differ in their implementation of equation 49. Building the $\alpha_{pol}$ matrix and inverting it directly to calculate the induced moments and polarization energy, as is done in the above equations, is one solution. A popular alternative is to solve for the induced moments in the following manner,

\[
p_{i}^{ind}(n) = p_{i}^{ind}(n-1) + \ddot{\alpha}_{i} \cdot (F + \sum_{j \neq i} T_{ij}^{p-p} p_{j}^{ind}(n-1))
\]

where $p_{i}^{ind}(n)$ represents the induced dipole vector on atom $i$ at iteration $n$, $\ddot{\alpha}_{i}$ its $3 \times 3$ atomic dipole polarizability tensor, $p_{j}^{ind}(n-1)$ the induced dipole vector on another atom $j$ at iteration $n-1$, $T_{ij}^{p-p}$ the tensor equation describing the interaction between the two, and $F$ an external uniform electric field. The fundamental idea of this equation is that one can apply an external electric field and allow the atomic induced dipoles in a molecule to couple to one another iteratively. At some iteration $(n)$ the induced dipole on any atomic site $i$ can be evaluated by adding together its induced dipole from the previous iteration $(n-1)$ with the product of its dipole polarizability $\ddot{\alpha}_{i}$ and the total electric
field including the uniform field and contribution of all other atoms \( j \) in the molecule from the previous iteration. One can evaluate the above equation for every atom in the molecule until self consistency in the induced dipoles is achieved to some pre-determined tolerance. Summing over all the converged atomic induced dipoles, one can obtain the molecular induced dipole which can be dotted into the external electric field to determine the polarization energy of the molecule. Finally, one could perform this calculation at various external field strengths and perform a finite difference, as was shown in section 2.3, to obtain the model molecular polarizability tensor. Equation 51 uses only atomic inducible dipoles, but this method could be extended to include fluctuating charges, though that is fairly uncommon in practice.
3.0 Progress Towards a One-Electron Model for the Non-valence Correlation-bound Anions of Polycyclic Aromatic Hydrocarbons

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3.1 Summary

A one-electron model Hamiltonian is used to characterize the non-valence correlation-bound (NVCB) anions of hexagonal polycyclic aromatic hydrocarbons (PAHs) $C_{6n^2}H_{6n}$ ($n = 3 - 7$). The model incorporates atomic electrostatic moments up to the quadrupole, coupled inducible charges and dipoles, and atom-centered repulsive Gaussians to describe the interaction between the excess electron and PAH. These model components are parameterized on and validated against all-electron calculations. Good agreement is found between the static dipole polarizabilities obtained from the model and those from PBE0 density functional theory and second-order Møller-Plesset perturbation theory calculations. In the model, charge flow dominates the in-plane polarizability of PAHs larger than $C_{54}H_{18}$, yielding an approximately quadratic scaling of the mean polarizability with the number of carbon atoms. Inclusion of electrostatic interactions decreases the EBEs for the largest PAHs considered by about 20% and shift charge distribution from above and below the plane of the ring system toward the periphery. Analysis of the electrostatic and polarization interactions provides insight into qualitative trends in the electron binding energy and the charge distribution of the lowest energy NVCB anion.
3.2 Introduction

Bound anions of molecules and molecular clusters can be divided into two main categories, valence and non-valence.\textsuperscript{90,91} Valence anions result from electron capture into energetically low-lying valence orbitals with the excess electron being localized near the molecular frame. Non-valence anions represent a distinctly different class where the excess electron is captured into a diffuse orbital with long-range interactions dominating the binding.\textsuperscript{4,5,90,92–94} In general, both electrostatics and long-range dispersion-like correlation can be important, but one of these may dominate over the other depending on the system. The two limiting cases are referred to as non-valence electrostatically-bound (NVEB)\textsuperscript{16,95–97} and non-valence correlation-bound (NVCB) anions. There is a growing body of experimental and theoretical studies of NVCB anions including fullerenes (e.g., $C_{60}$ and $C_{240}$) and their clusters ($C_{60}$)$_n$,\textsuperscript{12,14,24,29} certain water clusters,\textsuperscript{12,16,25,98–103} (NaCl)$_n$ clusters,\textsuperscript{23} Xe$_n$ clusters,\textsuperscript{9} $C_6F_6$\textsuperscript{1,4,104} and ($C_6F_6$)$_n$ clusters,\textsuperscript{6,105} and polycyclic aromatic hydrocarbons (PAHs).\textsuperscript{15}

The application of ab initio methods to NVCB anions presents a challenge because both an accurate treatment of electron correlation and the use of flexible basis sets are crucial. The correlation effects responsible for stabilizing NVCB anions are different from near degeneracy effects that arise from small HOMO-LUMO gaps. When starting from a Hartree-Fock (HF)\textsuperscript{106–108} reference in treating an NVCB anion, it is essential to include configurations that allow the orbital occupied by the excess electron to, “relax,” in response to dispersion-type correlation associated with configurations where the excess electron and a valence electron are both excited.\textsuperscript{16} By definition, NVCB anions are unbound in the HF approximation, and with the use of flexible basis sets containing diffuse functions, the excess electron occupies a discretized continuum (DC) orbital in the HF wavefunction. Methods that account for electron correlation, including second-order Møller-Plesset perturbation theory (MP2)\textsuperscript{109} and coupled cluster with single, double, and perturbative triple excitations (CCSD(T)),\textsuperscript{110} fail to recover the bound anion when starting from a HF reference wavefunction that has collapsed onto a DC level.\textsuperscript{16,25}

Density functional theory (DFT) methods based on the local density approximation (LDA) or the generalized gradient approximation (GGA) will fail to accurately describe NVCB states. The exchange-correlation density functional in such methods cannot describe the asymptotic, non-local
electron correlation that stabilizes NVCB anions. However, DFT functionals employing a non-local correlation potential show promise. Recently, it was shown that the van der Waals density functional rev-vdW-DF2 improves upon semi-local functionals in describing the image potential states (IPSs) of graphite, graphene, and carbon nanotubes. IPSs are unoccupied states lying between the Fermi level and the vacuum level of a solid, in which an excess electron can be trapped by an attractive long-range self-induced image potential. The underlying physics stabilizing IPSs, long-range electron correlation effects, is fundamentally the same as that leading to NVCB anions.

Electron affinity equation-of-motion coupled cluster with single and double excitations (EA-EOM-CCSD) and electron affinity equation-of-motion MP2 (EA-EOM-MP2), have been used frequently in past studies of NVCB anions. These methods are capable of accurately describing NVCB anions, but they are computationally demanding, $O(N^6)$ for canonical EA-EOM-CCSD and $O(N^5)$ for canonical EA-EOM-MP2, where $N$ is size of the orbital basis. There have been efforts made towards lowering the scaling of EOM-CCSD calculations. In particular, a nearly linear scaling version employing domain-based localized pair natural orbitals (DLPNO) has been introduced for evaluating ionization potentials and a quadratic scaling approach had been developed for electron affinities. However, the approximations that enable the low scaling can introduce errors on the order of tens to a hundred meV. While these are tolerable for ionization potentials, they are not acceptable for NVCB anions where binding energies are typically of the same order as these errors. The steep computational scaling of conventional EOM methods render them unsuitable for characterizing the NVCB anions of systems with hundreds to thousands of atoms.

An alternative approach to treating NVCB anions involves the use of a one-electron model Hamiltonian. The diffuse nature of non-valence anions allows one to make approximations in treating the interactions between the excess electron and the electrons of the molecule or cluster. These interactions involve electrostatics, dispersion, polarization, and exchange. The corresponding potentials in the model Hamiltonian are parameterized using the results of all-electron quantum mechanical (QM) calculations. The dispersion-like correlation effects present in a many-electron treatment can be recovered in a one-electron model upon integration of the excess electron’s degrees of freedom over a model polarization potential. The long-range electrostatic potential of the molecule can be described by atom-centered point multipoles. In past work electron exchange, charge penetration, and orthogonality have been accounted for via model potentials, similar in
spirit to the pseudopotentials which are used to approximate core electrons in electronic structure calculations.\textsuperscript{99–102} One-electron model Hamiltonians have been used to study the NVCB anions of spherical fullerenes and fullerene clusters composed of tens to hundreds of atoms\textsuperscript{12,14,29} Additionally, such models have been applied in theoretical studies of a solvated electron\textsuperscript{13,100–102} and water cluster anions.\textsuperscript{12,98,99} An inherent advantage of model approaches over all-electron ab-initio treatments, is the ability switch parts of the potential on and off. This affords insight into the magnitude and nature of different contributions to the binding of an excess electron.

This work studies the NVCB anions of hexagonal PAHs in the series $C_{6n}^2H_{6n}, n = 3 - 7$, using a one-electron model Hamiltonian implemented in the code PISCES.\textsuperscript{117} These hexagonal PAHs consist of a planar set of fused six member rings formed by an sp$^2$ hybridized network of carbon atoms. In a distributed multipole analysis, the edge carbon and hydrogen atoms have sizable atomic charges and dipoles due to the electronegativity difference of the atoms. However, the molecules are neutral and have no net dipole by symmetry, so the leading order molecular electrostatic moment is the quadrupole, $\Theta^{\text{mol}}$, moment. The only independent component of $\Theta^{\text{mol}}$ in a traceless Cartesian representation is that which is normal to the molecular plane $\Theta_{zz}^{\text{mol}}$, as $\Theta_{xx}^{\text{mol}} = \Theta_{yy}^{\text{mol}} = -\frac{1}{2} \Theta_{zz}^{\text{mol}}$. When described in terms of atomic multipoles, $\Theta_{zz}^{\text{mol}}$ has contributions from atomic quadrupoles $\Theta_{zz}$ largely associated with the carbon atoms as well as charges and dipoles arising from the edge C-H bonds.\textsuperscript{118} In a study employing EA-EOM-MP2, it was shown by Voora and Jordan that the charge density of the natural orbital occupied by the excess electron is somewhat localized around the periphery of PAHs such as hexabenzocoronene ($C_{42}H_{18}$).\textsuperscript{15} The authors attributed this to an attractive electrostatic interaction between the excess electron and the positively charged hydrogen atoms.

The work of Voora and Jordan\textsuperscript{15} was motivated in part by an experimental study performed by Craes et al. on the IPSs of nanostructures called graphene quantum dots (GQDs).\textsuperscript{119} GQDs are closely related to PAHs,\textsuperscript{120} as they can be made in a variety of shapes, sizes, and the edge carbon atoms can be terminated by hydrogen depending on the synthetic approach.\textsuperscript{121} Using scanning tunneling microscopy, Craes et al. mapped the spatial modulation of the local density of states corresponding to the first IPS of a hexagonal GQD with an area of 11 nm$^2$. The LDOS was dominated by a contribution with strong intensity at the center of the GQD and vanishing intensity at the edges. This contrasts the NVCB anions observed by Voora and Jordan, where the excess...
electron’s charge distribution localized near the edge C-H bonds of PAHs. One might expect that for sufficiently large PAHs with appreciable metallic character, the polarization potential stabilizing their NVCB anions would approach that which binds IPSs on GQDs producing a charge distribution that resembles the LDOS maps of Craes et al. However, the GQDs synthesized by Craes et al. were larger than the PAHs considered by Voora and Jordan, were likely terminated by unsaturated carbon atoms\textsuperscript{122} rather than hydrogen atoms, and there was an Ir(111) substrate supporting the nanoflakes. To the best of our knowledge there are no papers that perform a similar analysis on hydrogen-terminated GQDs. These factors make it difficult to compare theoretical results on gas phase NVCB anions to the experimental studies on IPSs of GQDs. A related question is whether or not the edge localization Voora and Jordan observed persists in the NVCB anions of PAHs larger than C\textsubscript{42}H\textsubscript{18}. Whether or not the edge localization is purely an electrostatic effect is an open question as well. Here we investigate these phenomena further using a one-electron model Hamiltonian.

The polarization potential in a model Hamiltonian treatment constitutes the crucial component, as it effectively accounts for the electron correlation responsible for stabilizing NVCB anions.\textsuperscript{116} This work makes use of Mayer and Åstrand’s model, which includes both atomic anisotropic dipole polarizabilities and fluctuating charges.\textsuperscript{69,70} The charge fluctuation method in the Mayer-Åstrand model is similar to that of Rappé and Goddard,\textsuperscript{71} which has been scrutinized due to its tendency to exaggerate polarization in insulating systems and unphysical behavior when molecular geometries deviate from equilibrium structures.\textsuperscript{80,81,123} The latter point is not an issue here as molecular geometries are taken to be rigid, but the former is worth considering. The accuracy of the model is assessed via comparison to polarization potentials and static dipole polarizabilities from all-electron calculations. Further analysis is performed by decomposing the model polarizabilities and polarization potentials into contributions from inducible dipoles and charge flow. Some QM methods struggle to accurately predict dipole polarizabilities in highly conjugated systems. An overshoot in dipole polarizabilities has been reported for conjugated molecular chains,\textsuperscript{124} 1D and 2D acenes, and 1D, 2D, and 3D H\textsubscript{2} clusters,\textsuperscript{125} as described by LDA and GGA density functionals. With this in mind, we calculate and compare reference dipole polarizabilities from HF,\textsuperscript{106–108} MP2,\textsuperscript{109} Coulomb-attenuating B3LYP (CAM-B3LYP),\textsuperscript{126} and PBE0.\textsuperscript{36} While CAM-B3LYP and PBE0 are based upon GGAs, both include some fraction of exact HF exchange making them less prone to
excess delocalization when compared to pure GGAs. CAM-B3LYP includes different fractions of
exact exchange at short-range and long-range with an error function smoothly connecting the two
regions.

This article serves as an in-depth study of the nature of the lowest energy NVCB anions of
hexagonal PAHs and a report on our progress in developing a one-electron model Hamiltonian
to describe them. In section 3.3.1, the one-electron model Hamiltonian is detailed. Section 3.3.2
describes the potential terms in the model Hamiltonian. Section 3.3.3 explains how the model
potential is parameterized and the process for obtaining reference polarization potentials, static
dipole polarizabilities, and electron binding energies (EBEs). Section 3.4.1 makes comparisons
between the model and reference polarizabilities for C_{6n}H_{6n}, where n = 1 – 7, and provides an
analysis of the charge flow and inducible dipole contributions to the in-plane and out-of-plane dipole
polarizabilities. A similar analysis is performed in section 3.4.2 for the polarization potentials. In
section 3.4.3 the quality of the of the full model potential is assessed via comparison to EA-EOM-
MP2 and EA-EOM-CCSD results for coronene (n = 2). Then, trends in EBE are reported in section
3.4.4 for the lowest energy NVCB anion of PAHs n = 3 – 7. In section 3.4.5 the full model potential
is dissected into contributions from electrostatics, polarization, and repulsion providing insight into
the impact of electrostatic effects. Additionally, density differences are reported in section 3.4.5 to
illustrate the effect electrostatics has on the excess electron’s charge distribution in these NVCB
states.

3.3 Methods

3.3.1 One-electron Model

The model Hamiltonian employed in this work for an excess electron interacting with a PAH is:

\[ \hat{H}(\mathbf{r}) = \hat{T}(\mathbf{r}) + \hat{V}_{es}(\mathbf{r}) + \hat{V}_{pol}(\mathbf{r}) + \hat{V}_{rep}(\mathbf{r}) \]  (52)

where \( \hat{T}(\mathbf{r}) \) is the kinetic energy operator for the excess electron and the operators \( \hat{V}_{es}(\mathbf{r}) \), \( \hat{V}_{pol}(\mathbf{r}) \),
and \( \hat{V}_{rep}(\mathbf{r}) \) represent, respectively, the electrostatic, polarization, and repulsion potential that the
excess electron experiences in the presence of the molecule. The molecule is treated as a fixed rigid body and the energy of the excess electron is evaluated on a real space 3D grid of points, \( \mathbf{r} \), using a sine-type discrete variable representation (DVR) basis.\(^{12,14}\) The construction of the sine DVR basis starts from particle-in-a-box (PIB) eigenfunctions of the form,

\[
\varphi_m(x) = \begin{cases} 
\sqrt{\frac{2}{L}} \sin \left( \frac{m\pi(x-x_0)}{L} \right) & -\frac{L}{2} \leq x \leq \frac{L}{2} \\
0 & \text{otherwise}
\end{cases}
\] (53)

where we represent them in one dimension, \( x \), for simplicity. In equation 53, \( L \) is the length of the box, \( x_0 \) corresponds to the edge \(-L/2\), and \( m \) a positive integer. In the case of three dimensions, the wavefunction is a product of sine functions for each Cartesian direction, i.e.,

\[
\varphi_{j,k,m}(x,y,z) = \varphi_j(x) \varphi_k(y) \varphi_m(z).
\]

The PIB functions given in equation 53 are eigenfunctions of the kinetic energy operator, but not of the potential energy operators. Discretizing the space in the box into a grid of evenly spaced points \( k = 0, 1, \ldots, n + 1 \), one can form another basis (again represented in one dimension for simplicity),

\[
u_j(x) = \sqrt{\frac{L}{n+1}} \sum_{k=1}^{n} \varphi_k(x) \varphi_k^{*}(x_j) \quad j = 1, 2, \ldots, n
\] (54)

where \( k = 0 \) and \( k = n + 1 \) correspond to the edges of the box and \( x_j \) refers to the coordinate of a particular grid point. Due to the orthogonality of the PIB eigenfunctions and the applied quadrature rule, the \( u_j(x) \) function is peaked at the grid point \( x_j \) and is zero at every other grid point. As a result, the potential matrix is diagonal in this representation. The kinetic energy is not diagonal in the \( \{u_j(x)\} \) basis, but is given by relatively simple analytical expressions.\(^{12}\)

### 3.3.2 Potential Terms

We describe the long-range electrostatic interaction of an electron with a molecule through the use of atomic multipoles. For each atom \( i \), we assign a permanent charge \( q_i \), dipole \( \mu_j \), and quadrupole \( \Theta_i \). This gives the following potential,

\[
V_{es}(\mathbf{r}) = -\sum_{i=1}^{N} \left( \frac{q_i}{R_{eff}^3} + \frac{\mu_i \cdot \mathbf{R}_{ie}}{R_{eff}^5} + \frac{\mathbf{R}_{ie} \cdot \Theta_i \cdot \mathbf{R}_{ie}}{R_{eff}^5} \right)
\] (55)
where $N$ is the number of atoms and $\mathbf{R}_{ie} = \mathbf{r} - \mathbf{R}_i$, i.e. the vector pointing from atom $i$ located at position $\mathbf{R}_i$ to the excess electron located at DVR grid point $\mathbf{r}$. The atoms are fixed during the simulation so the operator $V_{es}(\mathbf{r})$, and all other model Hamiltonian operators for that matter, are denoted as a function of only the excess electron’s position $\mathbf{r}$. Note that $\mu_i$ is a vector, $\bar{\Theta}_i$ a matrix, and the subscript $i$ designates that the multipoles are centered on atom, $i$. Short-range divergence in the electron-molecule electrostatic interaction is avoided by employing a damped distance function of the form,

\[
R_{\text{eff}} = \begin{cases} 
R_{ie} & R_{ie} \geq d \\
\frac{1}{2} + \left( \frac{R_{ie}}{d} \right)^3 \left( 1 - \frac{R_{ie}}{2d} \right) & R_{ie} < d
\end{cases}
\]  

(56)

where $R_{ie}$ is the magnitude of the vector between the electron and an atom. This effective distance damping is applied to the electron-molecule polarization interaction as well. The cutoff distance, $d$, differs for the electrostatic and polarization interactions, with the values being given in section 3.3.3. The same approach has been used in prior studies of NVNCB anions of fullerene and water clusters.\textsuperscript{12,14,29,98}

As mentioned previously, $V_{pol}(\mathbf{r})$ is based on the Mayer-Åstrand polarization model, in which each atom is assigned an inducible charge and an inducible dipole.\textsuperscript{70} The interactions between the inducible moments are damped to avoid divergence in the polarization energy at short distances. Note that this damping only applies to interactions between inducible moments, not the interaction between the excess electron and the inducible moments, which is handled by equation 56. To determine the induced moments in the model, the polarization energy is minimized subject to the constraint that the total molecular charge is conserved via a Lagrange multiplier.

The inducible charges and dipoles describe the response of the $\sigma$ and $\pi$ electrons to an external electric potential and field, polarizing within (charges and dipoles) and out (dipoles) of the molecular plane. The self-induced polarization potential the excess electron experiences at DVR grid point $\mathbf{r}$ is,

\[
V_{pol}(\mathbf{r}) = -\frac{1}{2} \left( \mathbf{F}^e(R_{\text{eff}}) \right)^T \cdot \bar{\alpha}_{pol} \cdot \mathbf{F}^e(R_{\text{eff}})
\]  

(57)

where $\mathbf{F}^e(R_{\text{eff}})$ is a supervector containing the potential and electric field of the excess electron at all atomic positions as well as the Lagrange multiplier used to conserve charge. The molecular polarization matrix, $\bar{\alpha}_{pol}$, contains the damped local interactions between induced multipoles, and
is obtained via the following inverted matrix:

\[
\bar{\alpha}_{pol} = \begin{pmatrix}
T_{q-q} & -T_{q-p} & 1 \\
-T_{p-q} & -T_{p-p} & 0 \\
1 & 0 & 0
\end{pmatrix}^{-1}
\]  

(58)

The entries \(T_{q-q}\), \(T_{p-p}\), \(T_{q-p}\), and \(T_{p-q}\) are tensor matrices containing the damped charge-charge, dipole-dipole, charge-dipole, and dipole-charge interaction equations respectively. Their dimensions are \(N \times N\), \(3N \times 3N\), \(3N \times N\), and \(N \times 3N\), respectively. The entries \(1\) and \(0\), represent a vector of ones of length \(N\) and of zeros of length \(3N\), respectively. The vector of ones is included to ensure that the overall charge of the system is constrained to be zero. Summing up the atomic contributions in \(\bar{\alpha}_{pol}\) yields the familiar \(3 \times 3\) molecular polarizability matrix \(\alpha_{mol}\).

The Mayer-Åstrand method presumes that atomic charge densities are well described by Gaussian distributions. This yields three free parameters for the atomic inducible moments: the charge width (\(R_q\)) which is related to chemical hardness and affects induced charges, the in-plane (\(\alpha_\parallel\)), and out-of-plane (\(\alpha_\perp\)) atomic dipole polarizabilities. There is a term for the dipolar width (\(R_p\)) of an atomic charge distribution in the Mayer-Åstrand model employed in the damping of the dipole-dipole, charge-dipole, and dipole-charge interactions. In their model, \(R_p\) is defined in terms of the atomic polarizability components \(\alpha_\parallel\) and \(\alpha_\perp\) in the following equation expressed in a.u.:70

\[
R_p = \left(\sqrt{\frac{2}{\pi}} \left(\frac{2}{\alpha_\parallel} + \frac{1}{\alpha_\perp}\right)^{-1}\right)^{1/3}
\]  

(59)

When fitting the parameters in the model to reproduce the static dipole polarizabilities obtained from electronic structure calculations, we found that when using this definition of \(R_p\), we could accurately reproduce the MP2 and PBE0 in-plane polarizabilities but underestimated the out-of-plane polarizabilities by as much as 19%. To address this limitation, we made the \(R_p\) of the carbon atoms a free parameter allowing it to vary along with the three other parameters for the carbon atoms, \(R_q\), \(\alpha_\parallel\), and \(\alpha_\perp\). This relaxation of the Mayer-Åstrand model was found to produce better molecular polarizabilities. The process for fitting all four parameters is detailed in section 3.3.3.
The potential capturing the short-range interactions, not described through the permanent multipoles and the polarization potential, of the excess electron with the atoms is of the form,

\[ V_{\text{rep}}(r) = \sum_{i}^{N} a \exp(-bR_{ie}^2) \]  

(60)

where the sum runs over each atom, \( i \), in the molecule. In this work, the same parameters \( a \) and \( b \) are used for both C and H. The value of \( b \) was carried over from previous work on fullerene structures and the process by which it was determined can be found in the SI of reference.\(^{14}\) The coefficient \( a \) was obtained by reproducing the EBE Voora and Jordan obtained for circumcoronene.\(^{15}\) The resulting repulsive potential accounts for the orthogonalization between the orbital occupied by the excess electron and the filled orbitals of the molecule. Additionally, charge penetration and exchange effects are implicitly folded into the potential.

3.3.3 Calculation Details

In this section, we describe the procedures used to parameterize the potentials of the one-electron model Hamiltonian described in section 3.3.2 and the QM calculations performed to measure the model results against. However, the entire parameterization process is summarized in figure 6 for the convenience of the reader.
Parameterization of model potential:

\[ \hat{H}(r) = \hat{T}(r) + \hat{V}_{\text{cs}}(r) + \hat{V}_{\text{pol}}(r) + \hat{V}_{\text{rep}}(r) \]

Figure 6: Summary of parameterization process for the model Hamiltonian. The process flows from the top box to the various steps as indicated by the arrows. Note that the reference numbers appearing in this image refer to the ordering in the published version. In this figure references [13], [17], and [29] correspond to references [14], [98], and [15] of this document.

The systems studied in this work are hexagonal PAHs in the \( \text{C}_{6n}^2\text{H}_{6n} \) series. The \( \text{sp}^2 \) carbon network is modeled after graphene (C-C bonds = 1.42 Å and C-C-C angles = 120°). Dangling C-C bonds present at the edges of the carbon nanoflakes were capped with hydrogen for the PAHs (C-H bonds = 1.09 Å and C-C-H angles = 120°).

In section 3.4.1 we compare the in-plane (\( \alpha_{xx/yy} \)) and out-of-plane (\( \alpha_{zz} \)) components of the static dipole polarizability obtained from the model to the results of PBE0, HF, MP2, and CAM-B3LYP calculations. The polarizabilities were obtained for the full series of PAHs considered using HF and PBE0, while MP2 and CAM-B3LYP results are reported for only the first four members, \( \text{C}_6\text{H}_6 \) to \( \text{C}_{96}\text{H}_{24} \). These calculations were performed in Psi4 v 1.4a2 or v 1.3.2 with default convergence criteria. To avoid linear dependency issues, symmetry-adapted, orthogonal combinations of atomic orbitals with overlap eigenvalues smaller than \( 10^{-7} \) were discarded. The def2-TZVPD orbital basis was used as it is optimized explicitly for dipole polarizabilities, is moderately diffuse,
and is designed to scale well with large molecular systems without introducing significant linear dependence.\textsuperscript{131} The Coulomb-exchange (JK) integrals were density fit in the SCF calculations with the def2-TZVP JK-fitting basis, which is also referred to as the def2-universal-JK fitting basis set in the literature.\textsuperscript{132} The integral transformations for the MP2 calculations used the def2-TZVPD resolution of identity fitting (RI a.k.a. MP2-fitting) basis.\textsuperscript{133} For the PAHs $C_6H_6 - C_{150}H_{30}$, the polarizabilities were obtained via a five-point stencil, first-order central difference of the induced dipole with a step size of $\pm 0.001$ a.u. in the electric field strength. For the last two members, $C_{216}H_{36}$ and $C_{294}H_{42}$, a three point stencil first-order central difference of the induced dipole with a step size of $\pm 0.002$ a.u. was used. The molecules were oriented such that the largest Abelian subgroup symmetry could be used in the presence or absence of an electric field perturbation: $D_{2h}$ when no field was applied and $C_{2v}$ when a field was applied along the x, y, or z axis. Figures 7a–7c illustrate the orientation for the first three members of the PAH series.

Figure 7: Orientation of molecules with respect to the axes along which electric fields are applied in static dipole polarizability calculations. The x and y axes correspond to $C_2$ rotational axes and the z-axis to the principal $C_6$ rotational axis. The molecules are centered on the origin. Image generated using VMD\textsuperscript{134}

Within our model the carbon atom’s charge flow parameter, $R_q$, atomic inducible dipole parameters, $\alpha$\textsubscript{||} and $\alpha$\textsubscript{⊥}, and dipole width, $R_p$, were fit to reproduce the PBE0/def2-TZVPD static dipole polarizability tensors for the series of PAHs, $C_6H_6$ to $C_{294}H_{42}$. The fitting process went as follows:
1. Fit $\alpha_\perp$ and $R_p$ to the out-of-plane component, $\alpha_{zz}$, from PBE0/def2-TZVPD.
2. Fix $\alpha_\perp$ and $R_p$ from the previous step and fit $\alpha_\parallel$ and $R_q$ to the in-plane components, $\alpha_{xx/yy}$, from PBE0/def2-TZVPD.

Steps (i) and (ii) were performed by using the non-linear least squares module, `least_squares`, of the SciPy Python library to minimize the sum of the residual errors between the model and PBE0 polarizability components.\textsuperscript{135} This yielded the following parameters $R_q = 0.4469 \, \text{a}_0$, $R_p = 1.6855 \, \text{a}_0$, $\alpha_\parallel = 10.1137 \, \text{a}_0^3$, and $\alpha_\perp = 13.6586 \, \text{a}_0^3$ for the carbon atoms. For the H atoms the isotropic dipole polarizabilities, $\alpha_\parallel = \alpha_\perp = 3.0172 \, \text{a}_0^3$ and $R_p = 0.9293 \, \text{a}_0$, developed by Mayer and Åstrand were used without further optimization.\textsuperscript{70} Also, charge flow was not permitted to or from the H atoms.

To further assess whether or not the value of $R_q$ was appropriate, we compared the induced charges obtained from the model for $\text{C}_{54}\text{H}_{18}$ to a Hirshfeld analysis\textsuperscript{54} of the PBE0/def2-TZVPD charge density when a uniform field of strength of 0.001 a.u. was applied along the x or y axis. The induced charges from the model were found to be in reasonable agreement with that of the Hirshfeld analysis, which was performed using Gaussian 16.\textsuperscript{136} This parameter set was used to calculate the dipole polarizability components of the PAH series $\text{C}_6\text{H}_6 - \text{C}_{294}\text{H}_{42}$. To determine the primary contributions to the in-plane ($\alpha_{xx/yy}$) polarizability the model calculations were performed using charge flow alone, inducible dipoles alone, and the combination of the two.

To assess the accuracy of the polarization model and the suitability of the parameter set, comparisons are made between the model, PBE0, and MP2 polarization potentials for $\text{C}_6\text{H}_6 - \text{C}_{96}\text{H}_{24}$ in section 3.4.2. HF values are also reported to allow for an assessment of the importance of correlation effects for the polarizabilities. In one set of calculations a point charge, $Q = -1 \, \text{e}$, was scanned above the center of the innermost carbon ring at distances of $z = 6.0 - 20.0 \, \text{a}_0$ with a step size of 2.0 $\text{a}_0$. In a separate set of calculations, the point charge was scanned within the molecular plane (xy) along the x-axis at distances of $x = 6.0 - 20.0 \, \text{a}_0$ from the edge of the PAH with a step size of 2.0 $\text{a}_0$. The MP2 scan proved to be expensive for the largest PAH, $\text{C}_{96}\text{H}_{24}$, so for this system only four distances in the scan along $z$ and $x$ were evaluated: 6.0, 10.0, 14.0, and 18.0 $\text{a}_0$. For even members in the PAH series ($n = 2 : \text{C}_{24}\text{H}_{12}$ and $n = 4 : \text{C}_{96}\text{H}_{24}$), the point charge traces a line that bisects the space between two hydrogen atoms capping the edges, while for odd members ($n = 1 : \text{C}_6\text{H}_6$ and $n = 3 : \text{C}_{54}\text{H}_{18}$) it approaches a hydrogen atom. For the electronic structure methods, the polarization potential was evaluated using the following formula,
\[ V_{\text{pol}}(R) = E^{Q+\text{PAH}}(R) - V_{\text{es}}^{\text{PAH}}(R) - E^{\text{PAH}} \]  

where \( E^{Q+\text{PAH}}(R) \) is the single point energy of a PAH in the presence of the point charge, \( Q \), fixed at distance \( R \) along \( x \) or \( z \), \( V_{\text{es}}^{\text{PAH}}(R) \) is the electrostatic potential of the PAH at \( R \), and \( E^{\text{PAH}} \) is the single point energy of the isolated PAH. We subtract \( V_{\text{es}}^{\text{PAH}}(R) \) as \( Q \) is negative point charge representing an excess electron. Figures 8a and 8b shows the axes along which the point charge is located for the first two members in the PAH series.

Figure 8: Depiction of point charge and acene arrangement in polarization scans for \( \text{C}_6\text{H}_6 \) and \( \text{C}_{24}\text{H}_{12} \). The yellow and blue spheres indicate the placement of the point charge at a distance of 6.0 \( a_0 \) and the arrows point from the origin to the point charge, illustrating how the distance is measured. The blue arrow and sphere represent the scans where the point charge is coplanar and the yellow set represents the scans perpendicular to the plane of atoms. The dashed red line between the hydrogen atoms of \( \text{C}_{24}\text{H}_{12} \) provides a visual indication of the origin from which \( x \) is measured for the coplanar scans of even members. The coplanar scans align with a \( C_2 \) rotational axis and the perpendicular scans align with the \( C_6 \) rotational axis. Image generated using VMD\textsuperscript{134}

In sections 3.4.3 and 3.4.4 we evaluate the success of the model in predicting the EBE of the lowest energy NVCB anion of the PAHs. In section 3.4.3 we evaluate the quality of the one-electron model when electrostatics and repulsion are introduced using a model system. Circumcoronene, \( \text{C}_{54}\text{H}_{18} \), is the smallest hexagonal PAH in the series \( \text{C}_{6n}^2\text{H}_{6n} \) for which Voora and Jordan identified a bound NVCB state.\textsuperscript{15} However, with a slight enhancement of nuclear charges
Coronene, $C_{24}H_{12}$, can be made to possess a bound non-valence anion. Nuclear-charge stabilization has been used in studies of the temporary (unbound) anions of $N_2^{−}$, the temporary polyanions of doubly- and triply-deprotonated naphthalenes, and the metastable dianion $SO_4^{2−}$. Coronene is a computationally tractable system affording treatment with both EA-EOM-MP2 and EA-EOM-CCSD. This provides an additional data point for assessing the performance of the model. We employed the modified Roos-ANODZ basis from Voora and Jordan’s study with frozen core orbitals, denoted as C(4s2p1d), H(4s3p), GH(6s6p3d)/5Å in their work. This basis includes a set of diffuse 6s, 6p, and 3d basis functions on ghost atoms 5Å above and below the central ring of coronene, which is denoted by GH(6s6p3d)/5Å. Binding energies were obtained using EA-EOM-MP2 and EA-EOM-CCSD at six nuclear scaling factors: 1.000125, 1.00016, 1.0002083, 1.00025, 1.0002916, and 1.0003. These scale factors correspond to excess molecular charges of 0.0195, 0.0260, 0.0325, 0.0390, 0.0455, and 0.0520 e, respectively. These calculations were performed using the CFOUR v2.1 package.

Due to the enhanced nuclear charges, $C_{24}H_{12}$ also possesses Rydberg states. If a sufficiently flexible basis set is used in the HF step of the EOM calculations, these appear as bound virtual orbitals, i.e. they are bound in the Koopmans’ theorem (KT) approximation. We show in section 3.4.3 that with the inclusion of electron correlation through the EOM procedure the lowest energy solution corresponds to the desired non-valence anion rather than a Rydberg state. Moreover, rather than presenting a problem, the presence of Rydberg states can be used as another performance check for the model Hamiltonian. Namely, comparison of the EBE predicted by the model without the contribution of polarization ($V_{rep,es}$) to the ab initio KT result, provides a test of the performance of the electrostatic and repulsive potential terms in the model Hamiltonian. However, even with the supplemental GH functions the modified Roos-ANODZ described in the previous paragraph, is not adequate for describing the highly extended Rydberg levels for the nuclear charges employed. Thus, the KT EBE values we report in this work were obtained using an even more diffuse 7s4p GH sets of functions, with s exponents as small as 0.0001105 for the two floating centers. These highly diffuse functions prove relatively unimportant for the lowest energy eigenvalue in the EA-EOM calculations, which is more strongly bound and more localized than the Rydberg states as described by the KT approximation.

Following the charge-scaled coronene calculations, we report in section 3.4.4 the binding
energies for the lowest energy NVCB state of acenes C\textsubscript{54}H\textsubscript{18} to C\textsubscript{294}H\textsubscript{42}. In all model calculations of the EBEs a common set of model parameters were employed, which are detailed here. The atomic charge and dipolar widths ($R_q$ and $R_p$) and dipole polarizability ($\alpha_\parallel$ and $\alpha_\perp$) parameters given earlier in this section were used to model the polarization of the PAHs in response to an excess electron. The cutoff for damping the interaction of the excess electron with inducible atomic multipoles, see equation 56, was set to $d = 5.70$ a\textsubscript{0}, which was taken from a previous study on fullerenes.\textsuperscript{14} To describe the short-range repulsive interactions between the excess electron and atoms via equation 60, the same coefficient, $a = 0.22705$, and exponential factor, $b = 0.200$, were used for the repulsive Gaussians on carbon and hydrogen atoms. To model the long-range electrostatic potential ($V_{es}$) of the PAHs, permanent atomic charges, dipoles, and quadrupoles were obtained via Gaussian distributed multipole analysis (GDMA)\textsuperscript{39} of the PBE0/cc-pVDZ charge density\textsuperscript{145} calculated using Gaussian 16.\textsuperscript{116} For C\textsubscript{24}H\textsubscript{12} the atomic charges from GDMA were modified to replicate the excess molecular charge present in the charge stabilized KT and EOM calculations described in the previous two paragraphs. For the larger PAHs considered, C\textsubscript{54}H\textsubscript{18} to C\textsubscript{294}H\textsubscript{42}, the nuclear charges were not enhanced. For both the charge-scaled coronene and charge-neutral PAH model calculations of EBE, the cutoff for damping the interaction of the excess electron with electrostatic atomic multipoles, see equation 56, was set to $d = 1.7724$ a\textsubscript{0}, which came from reference.\textsuperscript{98}

For the charge-scaled coronene calculations, the DVR box length was set to $L = 402$ a\textsubscript{0} containing a $200 \times 200 \times 200$ grid of points yielding a spacing of 2 a\textsubscript{0} between points. Section 3.4.3 reports the model binding energies for C\textsubscript{24}H\textsubscript{12} at all nuclear scale factors using the full ($V_{pol,rep,es}$) and the repulsion and electrostatic ($V_{rep,es}$) components of the one-electron model Hamiltonian. A box length of $L = 402$ a\textsubscript{0} was selected in this set of calculations to prevent artificial confinement of the highly extended Rydberg state wavefunction at the lowest values of nuclear charge scaling and in the absence of model polarization ($V_{rep,es}$). In the calculations modeling charge-neutral PAHs, C\textsubscript{54}H\textsubscript{18} to C\textsubscript{294}H\textsubscript{42}, we used a DVR box with side length $L = 251$ a\textsubscript{0} containing a $250 \times 250 \times 250$ grid of points yielding a spacing of 1 a\textsubscript{0} between points. This DVR box and grid size was selected to assure that the EBE of C\textsubscript{54}H\textsubscript{18}, with the most weakly bound NVCB anion, was well converged. Going to a larger DVR box length ($L = 301$ a\textsubscript{0}) with a 1 a\textsubscript{0} grid spacing, modified the binding of C\textsubscript{54}H\textsubscript{18} by 0.03 meV. In section 3.4.4, the model binding energies for PAHs C\textsubscript{54}H\textsubscript{18} to C\textsubscript{294}H\textsubscript{42} are reported for the model Hamiltonian with polarization alone ($V_{pol}$), with both polarization and
Having validated the model potential components and their parameterization in the preceding sections, we explore the edge localization of the lowest energy NVCB anion of the charge-neutral PAHs. In section 3.4.5, we plot one-dimensional slices of the interaction energy for C\textsubscript{54}H\textsubscript{18} and C\textsubscript{294}H\textsubscript{42}. These slices were obtained by scanning the energy at DVR grid points along the x axis at a fixed vertical separation, z, above the molecular plane. To gain an understanding of the role various potential components play in the binding of an excess electron in the charge-neutral PAHs, we plot slices of the individual model potential components, $V_{es}$, $V_{rep}$, and $V_{pol}$, and the combinations $V_{pol, rep}$, and $V_{pol, rep, es}$. To illustrate the impact of electrostatics on the charge density of the NVCB anions, we plot the difference in the excess electron density due to electrostatics in the model: \[ \Delta \rho(V_{es}) = \rho(V_{pol, rep, es}) - \rho(V_{pol, rep}) \] in section 3.4.5. The density differences were calculated using Multiwfn v3.7\textsuperscript{146} The isosurfaces are plotted for all charge-neutral PAHs studied at isovalues that correspond to 90\% enclosure of $\Delta \rho(V_{es})$.

### 3.4 Results & Discussion

#### 3.4.1 Model Validation: Polarizabilities

Accurately modeling the polarization response of the PAHs to an external electric field is the most important step in building a one-electron model for NVCB anions as it effectively accounts for the dispersion-type correlation responsible for stabilizing NVCB states. The polarization response of a molecule in the one-electron model is described via inducible atomic charges and dipoles. Methods employing charge equilibration techniques run the risk of overpolarizing molecules. This has been characterized in systems with insulating properties by an erroneous superlinear scaling of static dipole polarizability with system size.\textsuperscript{81,123} To establish the performance of the model, the in-plane and out-of-plane components of model and QM dipole polarizabilities are compared in figures 9a and 9b for PAHs C\textsubscript{6}H\textsubscript{6} – C\textsubscript{294}H\textsubscript{42}.
Figure 9: In-plane ($\alpha_{xx/yy}$) and out-of-plane ($\alpha_{zz}$) components of the static dipole polarizability (a.u.$^3$) for PAHs $C_{6n^2}H_{6n}$, $n = 1 - 7$, vs. the number of carbon atoms, $N_C$. The images on the left (a) report results obtained with the polarization model including induced charges only $q_{\text{ind}}$, dipoles only $\mu_{\text{ind}}$, and coupled induced charges and dipoles $q_{\text{ind}} + \mu_{\text{ind}}$, as well as the results of HF and PBE0 calculations. The images on the right (b) compare the polarizabilities from the full model with the results of HF, MP2, PBE0, and CAM-B3LYP calculations on the PAHs up to $n = 4$. Lines between points do not reflect fitted functions and are included for tracking trends in the data. Images generated using Matplotlib.$^{147}$
There are clear trends for the in-plane, $\alpha_{xx/yy}$, and out-of-plane, $\alpha_{zz}$, components of the polarizability as the number of carbon atoms, $N_C$, increases. The in-plane polarizability scales essentially quadratically with system size for all QM methods as well as the polarization model when charge flow is included. On the other hand, the out-of-plane polarizability exhibits, roughly, a linear scaling with system size for all methods considered. When considered individually, the point inducible dipole ($\mu_{\text{ind}}$) and the charge flow ($q_{\text{ind}}$) contributions to the model $\alpha_{xx/yy}$ become nearly equal for C$_{54}$H$_{18}$, with the charge flow contribution growing more rapidly with increasing system size. The net in-plane polarizability predicted by the full model ($q_{\text{ind}} + \mu_{\text{ind}}$) is less than the sum of the induced dipole and charge flow contributions when calculated separately due to the cross terms, $T_{q-p}$ and $T_{p-q}$, that couple the inducible dipole and charge-flow terms. A superlinear scaling of the in-plane component of hexagonal PAHs was observed in past work by Kirtman et al.. Different scaling for in-plane and out-of-plane polarizabilities has been observed in one-dimensional polyenes and linear acenes, as well as polythiophenes. The quadratic scaling of the in-plane components with system size indicates a growing conductive behavior brought about by electron delocalization within the $\pi$ system. The inclusion of charge-flow polarization in the model is crucial for capturing the increasing delocalization of $\pi$ electrons in the PAHs and concomitant growth in $\alpha_{xx/yy}$.

We now examine in more detail the polarizabilities obtained by the various QM methods. The $\alpha_{xx/yy}$ components obtained via methods including electron correlation (PBE0, CAM-B3LYP, and MP2) grow with molecular size somewhat faster than those obtained via HF. The CAM-B3LYP values are slightly smaller than those from PBE0 and MP2. For $\alpha_{zz}$, all methods considered give similar values. The agreement between the in-plane polarizabilities obtained from MP2 and PBE0 is surprising, since Kirtman et al. evaluated the $\alpha_{xx/yy}$ components of the dipole polarizability for hexagonal PAHs ($n = 1 - 5$) with B3LYP, MP2, and HF and found that the B3LYP values grew faster with system size than those from MP2 calculations. The authors calculated the ratio of $\alpha_{xx/yy}$ given by B3LYP to that of MP2 for C$_{96}$H$_{24}$ and obtained 1.0615. In the present study, the same ratio for PBE0 relative to MP2 is 1.0021. In fact, the ratio $\alpha_{xx/yy}(\text{PBE0}/\text{MP2})$ from our calculations is less than 1.01 for all PAHs studied with MP2. Additionally, we calculated the polarizability for C$_{96}$H$_{24}$ with B3LYP and found that $\alpha_{xx/yy}(\text{B3LYP}/\text{MP2}) = 1.0150$, which is an appreciably smaller ratio than that obtained by Kirtman et al. We attribute this discrepancy to the fact that our
calculations employed a much more flexible basis set than 3-21G,\textsuperscript{150} which was used by Kirtman et al.

The close agreement of the MP2 and PBE0 polarizabilities indicates that either method can be used as a reference for assessing the model polarizabilities. When both inducible atomic charges and dipoles are used in the model, \( q_{\text{ind}} + \mu_{\text{ind}} \), the polarizabilities are in good agreement with the PBE0 and the MP2 results. For \( \alpha_{xx/yy} \), the largest discrepancy between the model and the correlated \textit{ab initio} results occurs for corenene, for which the value predicted by the model is underestimated by \( \sim 6\% \). For \( \alpha_{zz} \), the largest discrepancy in the model occurs for benzene with an underestimation of \( \sim 7\% \) relative to MP2 and \( \sim 6\% \) relative to PBE0. The trends in how the polarizabilities evolve with increasing size of the PAH vary slightly for the model, PBE0, and MP2 methods, so there are PAHs for which the model overestimates or underestimates the reference values. However, the magnitude of the absolute errors are small relative to the size of \( \alpha_{xx/yy} \) and \( \alpha_{zz} \). These results indicate that the current model is sufficient for the qualitative/semi-quantitative explorations performed in this work.

3.4.2 Model Validation: Polarization

Next, we evaluate how well the model reproduces the polarization potential for a negative point charge interacting with the PAHs. We first consider the polarization potential when a point charge is scanned along the principal rotation axis of the PAHs. Figure 10 shows the results for the PAHs \( \text{C}_6\text{H}_6 \) to \( \text{C}_{96}\text{H}_{24} \).
Figure 10: Polarization potential (meV) for a point charge (Q = −1 e) at a distance of z (a₀) along the C₆ rotational axis of PAHs C₆n²H₆n (n = 1 − 4). Results are shown for HF, PBE0, and the polarization model. Model results are shown for \( V_{\text{pol}} \) using induced dipoles only, \( \mu_{\text{ind}} \), as well as coupled induced charges and dipoles, \( q_{\text{ind}} + \mu_{\text{ind}} \). Lines between points do not reflect fitted functions and are included for tracking trends in the data. Images generated using Matplotlib.¹⁴⁷

The polarization model closely reproduces the PBE0 and MP2 values of the polarization potential along the principal rotational axis except at short separations from the plane of the molecule. An interesting point of note is that the HF polarization potential tracks closely with those from the PBE0 and MP2 calculations as well. However, on the scale of the figure it is difficult to ascertain the percentage deviation of the model potential results from those obtained via electronic structure calculations at long-range. Table 1 reports the deviation of the model potential results from those of the HF, MP2, and PBE0 calculations by providing the percent changes.
Table 1: Percentage change of the \( q_{\text{ind}} + \mu_{\text{ind}} \) polarization potential relative to HF, PBE0\(^a\), and MP2\(^b\) for a point charge \( (Q = -1 \text{ e}) \) at a distance \( z \) (\( a_0 \)) along the \( C_6 \) rotational axis of PAHs \( C_{6n^2}H_{6n} \) \((n = 1 - 4)\).

<table>
<thead>
<tr>
<th>( z )</th>
<th>( C_6H_6 )</th>
<th>( C_{24}H_{12} )</th>
<th>( C_{54}H_{18} )</th>
<th>( C_{96}H_{24} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>9.8 [6.9] (7.7)</td>
<td>8.4 [7.4] (8.8)</td>
<td>8.7 [9.2] (10.6)</td>
<td>8.2 [9.5] (11.0)</td>
</tr>
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<td>8</td>
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<td>7.4 [6.2] (7.6)</td>
<td>7.6 [8.1] (9.4)</td>
<td>7.1 [8.6] (—)(^c)</td>
</tr>
<tr>
<td>10</td>
<td>10.8 [7.9] (8.7)</td>
<td>6.4 [5.1] (6.5)</td>
<td>6.3 [6.6] (7.9)</td>
<td>5.9 [7.4] (8.9)</td>
</tr>
<tr>
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<td>10.4 [7.6] (8.4)</td>
<td>5.9 [4.4] (5.7)</td>
<td>5.3 [5.3] (6.7)</td>
<td>4.8 [6.2] (—)</td>
</tr>
<tr>
<td>14</td>
<td>10.0 [7.4] (8.0)</td>
<td>5.7 [3.9] (5.3)</td>
<td>4.5 [4.4] (5.7)</td>
<td>4.1 [5.2] (6.7)</td>
</tr>
<tr>
<td>16</td>
<td>9.5 [7.0] (7.9)</td>
<td>5.5 [3.7] (5.0)</td>
<td>4.1 [3.7] (5.0)</td>
<td>3.5 [4.4] (—)</td>
</tr>
<tr>
<td>18</td>
<td>9.4 [6.8] (7.7)</td>
<td>5.4 [3.5] (4.8)</td>
<td>3.8 [3.2] (4.6)</td>
<td>3.0 [3.7] (5.2)</td>
</tr>
<tr>
<td>20</td>
<td>8.9 [6.9] (7.6)</td>
<td>5.3 [3.4] (4.8)</td>
<td>3.6 [2.8] (4.1)</td>
<td>2.7 [3.2] (—)</td>
</tr>
</tbody>
</table>

\(^a\) Percent change relative to PBE0 is in square brackets.
\(^b\) Percent change relative to MP2 is in parentheses.
\(^c\) — indicates that this reference value was not calculated.

From table 1 it is seen that in the case of a point charge approaching along the principal rotational axis, the model underestimates the magnitude of the polarization potential for all PAHs at all distances considered. The discrepancies between the model and PBE0 results are the largest at small point-charge PAH separations \( z < 10 \) where the percent changes relative to PBE0 vary from \(-9.5\) to \(-6.2\)% and for MP2 they vary from \(-11\) to \(-7.6\)%.

At longer range \( z \geq 10 \), the percent changes are somewhat smaller ranging from \(-7.9\) to \(-2.8\)% relative to PBE0 and from \(-8.9\) to \(-4.1\)% relative to MP2. When one considers the change in the in-plane charge distribution induced by a point charge located on the principal rotational axis, one sees that the leading induced molecular moment is the quadrupole, suggesting that to obtain better agreement with the results of the electronic structure calculations it may be necessary to extend the model to include atomic inducible quadrupole polarizabilities.

Figure 11, reports polarization potentials for the same systems when the point charge is coplanar...
with the molecule and scanned along a C$_2$ rotational axis (see figures 8a and 8b for visual depictions of the geometries).

Figure 11: Polarization potential (meV) for a point charge (Q = −1 e) at a distance x (a$_0$) along a C$_2$ rotational axis of PAHs C$_{6n}$H$_{6n}$ (n = 1 − 4). Results are shown for HF, PBE0, MP2, and the polarization model. Model results are reported for $V_{pol}$ using induced dipoles only, $\mu_{ind}$, as well as the full model with coupled induced charges and dipoles, $q_{ind} + \mu_{ind}$. Lines between points do not reflect fitted functions and are included for tracking trends in the data. Images generated using Matplotlib.$^{147}$

In this case, the model yields a potential that is more attractive than any of the QM methods at short range. At long range, the model underestimates the polarization potential from the PBE0 calculations and this is also true with respect to MP2 except for C$_{96}$H$_{24}$. The HF method tends to give a weaker in magnitude polarization potential than the model and correlated methods at all values of x with the exception of C$_{96}$H$_{24}$ where HF is slightly more polarized than MP2 at distances

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of $x = 6$ and $10 \, \text{a}_0$. As the system size grows, the separation between the $q_{\text{ind}} + \mu_{\text{ind}}$ and $\mu_{\text{ind}}$ model polarization potentials grows. This coincides with the trends in the $\alpha_{xx/yy}$ values given by $q_{\text{ind}}$ and $\mu_{\text{ind}}$ seen in figure 9a, where the contribution of charge flow increases more rapidly with system size. The percentage changes between the polarization potential from $q_{\text{ind}} + \mu_{\text{ind}}$ and the QM methods are tabulated in table 2.

Table 2: Percentage change of $q_{\text{ind}} + \mu_{\text{ind}}$ polarization potential relative to those from HF, PBE0\textsuperscript{a}, and MP2\textsuperscript{b} calculations for a point charge ($Q = -1 \, \text{e}$) at a distance $x$ ($\text{a}_0$) along one of the C\textsubscript{2} rotational axis of PAHs $C_{6n^2}H_{6n}$ ($n = 1 - 4$).

<table>
<thead>
<tr>
<th>$x$</th>
<th>$C_6H_6$</th>
<th>$C_{24}H_{12}$</th>
<th>$C_{54}H_{18}$</th>
<th>$C_{96}H_{24}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11.3 [8.4] (9.0)</td>
<td>9.0 [4.0] (5.3)</td>
<td>8.0 [3.0] (6.2)</td>
<td>3.9 [0.7] (8.8)</td>
</tr>
<tr>
<td>8</td>
<td>6.2 [3.6] (4.1)</td>
<td>5.8 [0.6] (1.7)</td>
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<td>3.3 [1.1] (—)\textsuperscript{c}</td>
</tr>
<tr>
<td>10</td>
<td>3.6 [1.2] (1.7)</td>
<td>4.1 [1.2] (0.4)</td>
<td>5.5 [0.9] (1.1)</td>
<td>3.8 [1.6] (4.1)</td>
</tr>
<tr>
<td>12</td>
<td>2.2 [0.2] (0.3)</td>
<td>3.1 [2.5] (1.7)</td>
<td>5.3 [1.6] (0.0)</td>
<td>4.6 [1.8] (—)</td>
</tr>
<tr>
<td>14</td>
<td>1.2 [0.9] (0.6)</td>
<td>2.3 [3.3] (2.7)</td>
<td>5.3 [2.0] (0.8)</td>
<td>5.4 [1.8] (2.1)</td>
</tr>
<tr>
<td>16</td>
<td>0.6 [1.4] (1.0)</td>
<td>1.8 [3.8] (3.3)</td>
<td>5.2 [2.3] (1.3)</td>
<td>6.1 [1.7] (—)</td>
</tr>
<tr>
<td>18</td>
<td>0.3 [2.1] (1.5)</td>
<td>1.4 [4.3] (3.7)</td>
<td>5.3 [2.6] (1.7)</td>
<td>6.7 [1.6] (1.0)</td>
</tr>
<tr>
<td>20</td>
<td>0.2 [1.9] (1.9)</td>
<td>1.3 [4.6] (4.0)</td>
<td>5.3 [2.8] (2.0)</td>
<td>7.2 [1.6] (—)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Percent change relative to PBE0 is in square brackets.

\textsuperscript{b} Percent change relative to MP2 is in parentheses.

\textsuperscript{c} — indicates that this reference value was not calculated.

In general, the percentage discrepancies of the model potential results relative to PBE0 and MP2 are smaller in magnitude than what was observed for the scan along the C\textsubscript{6} rotational axis. The percent change relative to PBE0 ranges from $-4.6$ to 1.2\% at long range. A similar trend is observed for the percent change relative to MP2, albeit with a larger span of, $-4$ to 4.1\% at long range. At the shortest distances considered, there is a growing discrepancy between the PBE0 and MP2 values of the in-plane polarization potential with increasing size of the PAH, with the MP2 value being about 7.5\% smaller in magnitude than the PBE0 result for $C_{96}H_{24}$. This disagreement is greater than the percentage difference between the MP2 and PBE0 values of the in-plane dipole polarizability and...
could reflect differences in these two theoretical methods for describing the molecular quadrupole polarizabilities.

3.4.3 Model Validation: Electrostatics and Repulsion

Having verified that the polarization model yields accurate polarizabilities and a reasonable polarization potential, we turn our attention to short-range repulsion and electrostatics. To assess the quality of the one-electron model when repulsion and electrostatics are included, comparisons are made to results at the KT level as well as EA-EOM-CCSD and EA-EOM-MP2 calculations on coronene with enhanced nuclear charges. Figure 12 plots the model Hamiltonian, KT, and EA-EOM values of the EBE as a function of the excess molecular charge.
Figure 12: Plot of the electron binding energy (EBE) of the lowest energy NVCB state of charge stabilized coronene against excess molecular charge ($Z_{ex}$). Note that a positive EBE indicates that the anion is bound. The plot includes the EBE obtained via EA-EOM-CCSD, EA-EOM-MP2, Koopmans’ Theorem (KT), and the model Hamiltonian. The EBEs of EA-EOM-CCSD, EA-EOM-MP2, and model Hamiltonian with polarization, $V_{pol,rep,es}$, are fit by linear functions of $Z_{ex}$, while the KT and model Hamiltonian without polarization $V_{rep,es}$ results are fit to curves proportional to $Z_{ex}^2$. The legend of the figure shows the fit coefficients for each data set. Image generated using Matplotlib.

As noted in section 3.3.3, the scaling of atomic charges of coronene introduces a long-range Coulomb potential, which binds Rydberg states so long as sufficiently flexible basis sets are used. In the absence of correlation effects in the ab initio calculations (KT) and the one-electron model without polarization, $V_{rep,es}$, the bound states are necessarily Rydberg in nature. However, it is not obvious a priori whether the lowest energy state bound in EA-EOM or the one-electron model including polarization, $V_{pol,rep,es}$, will be Rydberg, NVCB, or a strongly mixed state. Regardless
of the nature of this state, this provides additional data points for assessing the performance of the model when polarization effects are included.

We consider first the binding energies in the absence of correlation/polarization effects. The ab initio KT EBEs and the corresponding model potential results, $V_{rep,es}$, are in excellent agreement. This validates the description of the electrostatics and the short-range repulsion in the model. In addition, these EBEs show a quadratic dependence on $Z_{ex}$, consistent with the ground state being Rydberg in nature.\textsuperscript{151} On the other hand, the EBEs calculated using the EA-EOM methods or the full model potential, $V_{pol,rep,es}$, display a near linear dependence on $Z_{ex}$ indicating that these correspond to non-valence anions (stabilized by the addition of the Coulomb potential) rather than Rydberg states. Again, for testing the performance of the model, which of these interpretations is more correct is not particularly relevant.

Note that for charge-enhanced coronene, the model with polarization ($V_{pol,rep,es}$), underestimates the EA-EOM EBEs by as much as 20%. Factors contributing to this include the fact that the model underestimates the PBE0 in-plane polarizability by $\sim 6\%$ and also that the use of a 2 bohr spacing of the DVR grid introduces errors of $\sim 5.6\%$ on average in the binding energy of the NVCB anion of coronene with enhanced nuclear charge. We do not find this particularly concerning because we are targeting the NVCB anions of the larger charge-neutral PAHs where the error of the model polarizabilities with respect PBE0 and MP2 are smaller. The agreement between the KT and model $V_{rep,es}$ EBEs demonstrates what we had hoped to find with this data set, namely the model electrostatics and repulsion is performing well.

### 3.4.4 Binding Energies of Charge-Neutral PAH NVCB Anions

Next, we report the EBEs of the ground state NVCB anion of PAHs $C_{54}H_{18}$ to $C_{294}H_{42}$. Table 3 reports the EBEs for $V_{pol}$ as well as the $V_{pol,rep}$ and $V_{pol,rep,es}$ combinations of the model potential components.
Table 3: Electron binding energy in meV for the lowest energy NVCB state for PAHs $C_{6n^2}H_{6n}$ ($n = 3 - 7$) for the model Hamiltonian with polarization alone ($V_{pol}$), with both polarization and repulsion ($V_{pol,rep}$), and the full potential including electrostatic charges through quadrupoles on all atoms ($V_{pol,rep,es}$).

<table>
<thead>
<tr>
<th>PAH</th>
<th>$V_{pol}$</th>
<th>$V_{pol,rep}$</th>
<th>$V_{pol,rep,es}$</th>
</tr>
</thead>
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<td>$C_{54}H_{18}$</td>
<td>2042.9</td>
<td>12.2</td>
<td>12.3</td>
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<tr>
<td>$C_{96}H_{24}$</td>
<td>2370.3</td>
<td>55.8</td>
<td>49.2</td>
</tr>
<tr>
<td>$C_{150}H_{30}$</td>
<td>2581.1</td>
<td>113.8</td>
<td>93.8</td>
</tr>
<tr>
<td>$C_{216}H_{36}$</td>
<td>2727.8</td>
<td>173.1</td>
<td>139.1</td>
</tr>
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<td>$C_{294}H_{42}$</td>
<td>2835.6</td>
<td>227.1</td>
<td>182.8</td>
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</tbody>
</table>

As can be seen from the results reported in table 3, polarization and repulsion are the largest contributions in magnitude to the total binding energy, with the repulsive potential greatly reducing the EBEs obtained using the polarization component alone. Electrostatics are less important relative to the contributions of polarization and repulsion to the EBEs, but do lead to non-negligible reductions of the EBEs of the three larger PAHs, with the largest reduction being $\sim 20\%$. The EBE of $C_{54}H_{18}$ when using the full model potential ($V_{pol,rep,es}$) is 12.3 meV, which is in good agreement with Voora and Jordan’s EA-EOM-MP2 result of 12.6 meV.15

3.4.5 Understanding Edge Localization: Potential Slices and Density Differences

As noted in the previous section, the model closely reproduces the EA-EOM-MP2 binding energy for $C_{54}H_{18}$. However, this is not surprising as the parameters in the repulsive potential were chosen so as to give this outcome. We have also shown that this choice of the repulsive parameters performs reasonably well for the charge enhanced $C_{24}H_{12}$ species. We note also that for other systems (e.g., water clusters) it has been established the values of the repulsive parameters determined on one size cluster, gives quantitatively accurate EBEs when applied to a wide range of other water clusters (for which EOM calculations are possible to check the performance of the model).98,103
Having established the above points, there are two questions that have yet to be addressed. Is the edge localization reported by Voora and Jordan for the ground state NVCB anion of $C_{54}H_{18}$ purely an electrostatic effect, and does this behavior persist for appreciably larger PAHs? To answer these questions, we plot for $C_{54}H_{18}$ and $C_{294}H_{42}$ one-dimensional slices along the $x$ axis for the interaction between the excess electron (modeled via a negative point charge) with the following potential components: $V_{pol}$, $V_{rep}$, and $V_{es}$, as well as the combinations $V_{pol,rep}$ and $V_{pol,rep,es}$. Slices are taken at four values of $z$ above the plane of the ring systems to illustrate how the interaction changes with vertical separation of the excess electron from the PAHs. Figures 13a–13h show the results.
Figure 13: One-dimensional slices of the model potential for a negative point charge (e\textsuperscript{−}) interacting with C\textsubscript{54}H\textsubscript{18} (a,c,e,g) and C\textsubscript{294}H\textsubscript{42} (b,d,f,h). All images represent a slice along x axis. The distance of the slice above the plane of atoms (z) is fixed at the value indicated by the text at the bottom of each plot. Each set of images shows the potential due to polarization alone (\( V_{\text{pol}} \)), repulsion (\( V_{\text{rep}} \)), electrostatics (\( V_{\text{es}} \)), both polarization and repulsion (\( V_{\text{pol},\text{rep}} \)), and the full model potential employing electrostatic charges through quadrupoles on all atoms (\( V_{\text{pol},\text{rep},\text{es}} \)). Images generated using Matplotlib.\textsuperscript{147}
Inspecting the slices of the individual potential components for C$_{54}$H$_{18}$ and C$_{294}$H$_{42}$ one sees that the electrostatic potentials ($V_{es}$) are primarily repulsive above the plane of the atoms, i.e. $-11 < x < 11$ and $-24 < x < 24$ $a_0$ for C$_{54}$H$_{18}$ and C$_{294}$H$_{42}$ respectively. At the shortest distance considered, $z = 2.5$ $a_0$, both the repulsive potentials ($V_{rep}$) and $V_{es}$ display oscillations as one scans across the surface. Although, $V_{es}$ oscillates between negative and positive values at $z = 2.5$ $a_0$, the average electrostatic potential is repulsive in this region. These fluctuations weaken for vertical separations of $z > 2.5$ $a_0$ due to its short-range nature. By $z = 6.5$ $a_0$, the effects of $V_{rep}$ are negligible making $V_{es}$ and $V_{pol}$ the dominate contributions, which is to be expected. A key finding is that $V_{es}$ is repulsive above and below the plane of the molecules, but it is attractive outside the plane of atoms, $|x| > 11$ and $|x| > 24$ $a_0$ for C$_{54}$H$_{18}$ and C$_{294}$H$_{42}$ respectively, with the deepest point in $V_{es}$ appearing in this region for each value of $z$ considered. The behavior of the electrostatic potential makes non-negligible modifications to the shape of full model potential $V_{pol,rep,es}$, that lowers the probability of the excess electron occupying space above and below the plane of atoms and increases the probability of the electron localizing near the C-H bonds. These observations indicate that the edge localization observed by Voora and Jordan is an electrostatic effect as they had conjectured.

One attribute distinguishing the electrostatic potentials of C$_{54}$H$_{18}$ and C$_{294}$H$_{42}$ is the magnitude of $V_{es}$. For $z \geq 4.5$ $a_0$, the electrostatic interaction above the plane of atoms is less repulsive for C$_{294}$H$_{42}$ than C$_{54}$H$_{18}$. At $z = 4.5$ $a_0$, the electrostatics and repulsion above C$_{294}$H$_{42}$ is weak enough relative to polarization that $V_{pol,rep,es}$ is more attractive at the center than at the edges of the PAH. This can be attributed to, in part, the vanishing of atomic charges and dipoles on the central carbon atoms with increasing system size, as the impact of the edge C-H bonds on the atomic electrostatic moments is smallest at the center of these PAHs.

The potential slices in figures 13a–13h demonstrate that the electrostatic potential is repulsive above and below the $\pi$ system and introduces attractive potential wells along the edges. To clearly illustrate the impact of electrostatics on the electronic density we plot the change in electronic density of the lowest energy NVCB state of the PAHs when electrostatics are introduced into the model Hamiltonian, i.e. $\Delta \rho (V_{es}) = \rho (V_{pol,rep,es}) - \rho (V_{pol,rep})$. Figure 14 depicts the density differences for PAHs C$_{6n^2}$H$_{6n}$ ($n = 3 - 7$).
Figure 14: Change in electronic density due to electrostatics for the lowest energy NVNCB anion of PAHs $C_{6n^2}H_{6n}$ ($n = 3 - 7$). The results were obtained by calculating the electronic density of the NVNCB anion while employing the full model potential $V_{pol, rep, es}$ and subtracting the density obtained in the absence of electrostatics $V_{pol, rep}$, i.e. $\Delta \rho(V_{es}) = \rho(V_{pol, rep, es}) - \rho(V_{pol, rep})$. Each column reports results for a different PAH as indicated by the number at the top of the image (e.g. $C_{6n^2}H_{6n}$ ($n = 3$) is $C_{54}H_{18}$). Two perspectives of the same plot are shown for each PAH with labels of, “z,” or, “y”. The top row of density difference plots denoted as, “z,” in the figure are oriented along the $C_6$ rotational axis and the bottom row of plots denoted as, “y,” in the figure are oriented along one of the $C_2$ rotational axis. The surfaces are drawn at an isovalue such that they enclose 90% of the change in the excess electron’s charge density. Voids in the density difference appearing as white space are portions that would be captured at smaller isovalues. Blue coloration indicates a decrease in electronic density and red coloration indicates an increase in electronic density. Images generated using VMD.$^{134}$

For all PAHs considered the region of space above and below the $\pi$ system experience a decrease in electron density, whereas there is a buildup of electron density around the perimeter of the PAHs upon the inclusion of electrostatics. This illustrates that the electrostatics make non-trivial changes to the charge distribution of the NVNCB states of PAHs and that the edge localization of the single particle orbitals is a consequence of electrostatics, just as Voora and Jordan had conjectured.
Furthermore, the density differences show that preferential binding at the edges persists for larger PAHs, which consistent with the behavior of $V_{\text{pol, rep, es}}$ observed in figures 13a–13f.

### 3.5 Conclusions

This work presents progress towards a one-electron model in the code PISCES, aimed at treating NVCB anions of large hexagonal PAHs with molecular formula $\text{C}_{6n^2}\text{H}_{6n}$ where $n = 3, 4, 5, \ldots$ The results provide insight into the nature of the NVCB anions of these molecules, which would be inaccessible to high accuracy ab initio QM methods such as EA-EOM-CCSD. The one-electron model Hamiltonian employed in this work allows us to inspect the contributions of polarization, repulsion, and electrostatics to the NVCB anions. In doing so, we assessed the impact of electrostatics on the electron binding energy and charge distribution of the orbital associated with the excess electron.

Good agreement was observed between the dipole polarizabilities of the model and those from PBE0 and MP2 calculations. Charge flow polarization is found to dominate the model in-plane polarizability components ($\alpha_{xx/yy}$) of PAH systems above $\text{C}_{54}\text{H}_{18}$. We compared scans of the polarization potential obtained from model calculations against results from MP2 and PBE0 calculations. Modest discrepancies were observed relative to MP2 and PBE0. These discrepancies tend to decrease at larger separations between the point charge and PAHs. The model underestimates the magnitude of the polarization potential when a point charge is perpendicular to the plane of atoms. It is our current belief that this is the result of higher order polarizabilities not explicitly accounted for in the model, which we plan to explore in future work.

It was shown that inclusion of electrostatics reduces the binding energy of the ground state NVCB anions of the larger hexagonal PAHs studied by up to 20%. In addition, the inclusion of electrostatics shifts the charge density of the excess electron toward the periphery of the ring systems. Future work includes a more rigorous parameterization of the repulsive Gaussians using reference EOM calculations on the ground and first electronically excited NVCB anions of larger PAHs.
3.6 Acknowledgements

This work was supported by National Science Foundation grant CHE-1762337 and computational resources made available by the University of Pittsburgh Center for Research Computing. We thank Tae Hoon Choi for his aid in developing the one-electron model Hamiltonian used for PAHs in PISCES and Jakub Brzeski for sharing his unpublished Koopmans’ theorem data with us. There are no conflicts of interest to report.

3.7 Data Availability Statement

The data that support the findings of this study are openly available at the following URL/DOI: https://github.com/dmm219/NVCB_ES_VdW_Volume.
4.0 A Practical Electrostatic Model for Hexagonal Polycyclic Aromatic Hydrocarbons and Carbon Nanoflakes: Implications for Graphene

This work was performed in collaboration with Dr. Alston Misquitta and Dr. Michael Rutter. My contributions to this work include: calculating distributed multipoles, construction of an electrostatic model for large polycyclic aromatic hydrocarbons, evaluating model and all-electron electrostatic potentials, generating tables and figures, as well as the writing and editing of portions of the manuscript. The manuscript is in preparation with plans to be submitted to The Journal of Physical Chemistry Letters.

4.1 Summary

It is generally assumed that the central carbon atoms of large hexagonal polycyclic aromatic hydrocarbons as well as the carbon atoms of graphitic samples have sizable (\(-0.6\) to \(-1.2\) a.u.) quadrupole moments. In this work we call that assumption into question and suggest that a near-zero value of the atomic quadrupole moment of the carbon atoms in these systems is more appropriate. In this interpretation the net quadrupole moment of finite graphene and graphitic samples are dominated by edge dipoles.

4.2 Main Body

Electrostatics play a fundamental role in a wide range of processes including intermolecular interactions, surface adsorption, and crystallization. An accurate description of electrostatics is important in simulating these and other chemical and biological processes using force fields. Most force fields used in the simulation of complex systems treat electrostatics through atomic point charges, but increasingly, force fields are employing atomic multipoles through the quadrupole (and higher) to provide a more realistic description of the electrostatics outside of the overlap
It is well known that atomic multipoles are not observable experimentally, and different theoretical approaches can lead to appreciably different values.

In this work, we revisit the problem of the atomic multipoles of hexagonal polycyclic aromatic hydrocarbons (PAHs). These species have been the subject of several studies \cite{jenness19,hesselmann20,jordan21} that used Gaussian distributed multipole analysis (GDMA)\cite{gdma} to calculate atomic multipoles. In part, these earlier studies were motivated by a desire to use the multipoles of the PAHs in an extrapolation procedure to estimate the out-of-plane component of the quadrupole moment of a carbon atom ($Q_{20}$) in graphene. However, there are issues with how GDMA handles overlap.\cite{overlap_issues,overlap_issues2} For this reason, we decided to calculate the multipole moments of hexagonal PAHs up to C$_{96}$H$_{24}$ in size using the basis set iterative Stockholder analysis (BS-ISA)\cite{bs isa} method which addresses this limitation. While atomic multipoles are not observables and depend on the computational method employed, we adopt simple criteria for determining which set of atomic multipoles is, “more correct”. Namely, the multipolar expansion should converge rapidly to an accurate representation of the electrostatic potential at intermediate to large separations (i.e., outside the region of charge penetration). What we seek is a minimal, realistic model of electrostatics with these criteria guiding our assessment.

In the prior theoretical studies of Jenness and Jordan,\cite{jenness19} Heßelmann,\cite{hesselmann20} and Jordan and Heßelmann\cite{jordan21} the GDMA procedure was used to determine atomic moments from the charge distribution of DFT calculations on hexagonal PAHs up to C$_{96}$H$_{24}$ in size. These studies showed that the values of atomic charges and dipoles associated with the C atoms of the central ring rapidly converge to zero while the value of $Q_{20}$ converged to a finite negative value with increasing size of the PAH. In fact, the moments on the central atom are well converged at circumcoronene, C$_{54}$H$_{18}$, indicating that in the GDMA approach the edge CH bonds have little impact on the charge distributions of the interior atoms. It was further assumed in these studies that the value of obtained in this manner pertains also to graphene.

In this work we calculate the atomic moments of the benzene (C$_6$H$_6$), coronene (C$_{24}$H$_{12}$), circumcoronene (C$_{54}$H$_{18}$), and dicircumcoronene (C$_{96}$H$_{24}$) sequence of hexagonal PAHs using BS-ISA. These calculations were carried out using the asymptotically corrected\cite{pbe0} PBE0 density functional method,\cite{pbe0,pbe0,pbe0,pbe0} denoted here as PBE0(AC), together with the aug-cc-pVTZ basis.\cite{aug_cc,pbe0} For comparison, atomic multiples were also calculated using the GDMA procedure as applied to the PBE0(AC)/aug-cc-pVTZ charge densities. Additional details concerning these calculations are given...
in the supporting information document. The atomic charges, magnitudes of the atomic dipoles and the quadrupole components of the innermost C atoms of benzene through dicircumcoronene are summarized in Table 4.

The moments for the other atoms are reported in the supporting information document. The most relevant result is the finding that for the central carbon atoms of dicircumcoronene the BS-ISA procedure gives a $Q_{C_{20}}$ value of only $-0.006$ a.u., which is nearly 200 times smaller in magnitude than that obtained from the GDMA calculations. It is important to note that the molecular quadrupoles from GDMA and BS-ISA both closely reproduce those of the PBE0(AC) calculations for the PAHs considered. However, while in the GDMA procedure the molecular $Q_{C_{20}}$ values are dominated by the atomic quadrupoles, in the BS-ISA they are dominated by the dipole moments associated with the edge CH groups.

Table 4: Average atomic charges, atomic dipoles (magnitudes) and $Q_{C_{20}}$ quadrupole moments on the central carbon atoms in the $C_{6n^2}H_{6n}$, $n = 1$ – 4 PAHs. All moments are in atomic units.

<table>
<thead>
<tr>
<th>PAH</th>
<th>BS-ISA</th>
<th>GDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q^C$</td>
<td>$\mu^C$</td>
</tr>
<tr>
<td>$C_6H_6$</td>
<td>-0.126</td>
<td>0.056</td>
</tr>
<tr>
<td>$C_{24}H_{12}$</td>
<td>-0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>$C_{54}H_{18}$</td>
<td>0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>$C_{96}H_{24}$</td>
<td>-0.001</td>
<td>0.001</td>
</tr>
</tbody>
</table>

We now raise the question as to whether there is a compelling reason for preferring the BS-ISA moments over the GDMA values? Obviously, experiments cannot establish the values of the atomic quadrupoles, nor can they inform us whether the net quadrupole moment is dominated by atomic quadrupoles on the C atoms or by the edge dipoles. One criterion that is useful in addressing this question is the rate of convergence with increasing rank of the multipole expansion to the exact electrostatic potential. Figure 1 reports the electrostatic energy of a negative point charge interacting with $C_{96}H_{24}$ when it is scanned along the principle rotational axis of the molecule. Results are reported for the PBE0(AC) charge density and for the GDMA, and BS-ISA multipole expansions at successively higher order atomic multipolar ranks. Additional details for these calculations are provided in the supporting information document.
Figure 15: Convergence of multipolar electrostatic interaction energy when a negative point charge is scanned along the principle rotation axis of dicircumcoronene. The value of $\ell$ in the legends indicates the highest rank atomic multipole in the expansion. The top image (a) shows the interaction energies for $2 \leq z \leq 12$ Å with the insets showing short-range energy for the PBE0(AC) charge density and $\ell = 2, 3, 4$ multipole expansions; the middle image (b) shows the difference between the interaction energies from the multipole expansions and that obtained directly from the PBE0(AC) charge density for $z \geq 4$ Å for which charge penetration is unimportant, and the bottom image (c) shows the natural log of the magnitude of difference between the interaction energies from the multipole expansions and that obtained directly from the PBE0(AC) charge density for $2 \leq z \leq 4$ Å. Linear fits to the data are included.
Figure 15a presents the differences between the energies obtained from the various GDMA and BS-ISA multipole expansions and the, “exact,” PBE0(AC) results for point charge-PAH separations (z) between 2 and 12 Å. The turnover near 3 Å in the electrostatic potential from the PBE0(AC) calculations is due to charge penetration, which is absent from the electrostatic potentials of the multipole expansions. From Figure 15b, it is seen that at distances where charge penetration is negligible, the electrostatic potential from the BS-ISA calculations is already well converged by atomic charges, dipoles, and quadrupoles ℓ = 2. In fact, BS-ISA even when truncated to include only atomic charges, gives a reasonably accurate representation of the electrostatic interaction energy. In contrast, with the GDMA procedure it is necessary to include moments through the hexadecapole ℓ = 4 to obtain well converged results. The electrostatic potentials from the ℓ = 2 and ℓ = 3 GDMA expansions differ significantly from the PBE0(AC) result. The very small error in the BS-ISA electrostatic potential over this range of distances when including terms through ℓ = 4, is expected to be due to the errors introduced by use of density fitting basis sets.

At distances shorter than 4 Å, where charge penetration is important, the electrostatic potentials from BS-ISA and GDMA differ appreciably from the PBE0(AC) result. The BS-ISA calculations yield an interaction less attractive than PBE0(AC), while the opposite is true of the GDMA calculations (see inset of Figure 15a). For the negative test charge used in our calculations, charge penetration is attractive. Thus, at short range, the electrostatic potentials predicted by BS-ISA show the expected behavior while those from GDMA are unphysical. In the region that charge penetration is important, the deviation of the electrostatic potentials from a multipole expansion from the DFT results should show an exponential distance dependence. As seen in Figure 1c, the deviation of the electrostatic potentials from the BS-ISA multipole expansions from that of PBE0(AC) displays the expected exponential distance dependence at short range, with nearly the same results whether the expansion is truncated at ℓ = 2, ℓ = 3, or ℓ = 4. The situation is very different in the case of the GDMA expansion. Not only is the sign of this energy difference incorrect, the GDMA electrostatic potential over this distance range depends sensitively on the order of the expansion. Thus, at distances where charge penetration is relatively unimportant, the BS-ISA multiple expansion converges much more rapidly than the GDMA expansion, and at distances where charge penetration is important BS-ISA, unlike GDMA, displays physically correct behavior. This analysis lends support to the conclusion that the multipole moments from BS-ISA are more realistic than those from GDMA.
Both GDMA and BS-ISA partition the reference charge distribution to determine atomic multiple moments. An alternative approach is to least squares fit the moments to the electrostatic potential. This approach has been applied to benzene for which it gives an \( Q_{20}^C \) value of \(-0.06\) a.u.\(^{161}\) compared to the GDMA and BS-ISA values of \(-1.137\) and 0.007 a.u., respectively. Thus, the electrostatic fitting approach, like the BS-ISA procedure, predicts that the quadrupole moment of benzene derives primarily from the CH bond dipoles.

We now consider the implications of these results at the scale of experimental samples of graphene nanoflakes, which span a few nanometers up to a micrometer. One can envision an experiment in which one measures the net quadrupole moment, \( Q_{20} \), of a finite graphene nanoflake and then divides by number of carbon atoms in the sample to obtain a value for the atomic moment, \( Q_{20}^C \). Although such a measurement has not been carried out on a graphene nanoflake, Whitehouse and Buckingham (W&B) used this strategy to determine a carbon atom in graphite reporting a value of \(-0.675\) a.u.\(^{162}\) One could reasonably expect graphene and graphite to have similar values for \( Q_{20}^C \) and the W&B value has been used in several force field simulations of molecular adsorption on both graphite and graphene.\(^{118,163–165}\) We note that the W&B value of \( Q_{20}^C \) is about 40\% smaller in magnitude than the GDMA value determined from the calculations on the PAHs and is about two orders of magnitude larger than the corresponding BS-ISA result.

With regard to the electrostatic potential of graphene, it is important to note that the potential above (or below) the middle of a hexagonal lattice of atomic quadrupole moments approaches zero with increasing size of the lattice.\(^{118,166}\) This indicates that the value of \( Q_{20}^C \) is inconsequential for the electrostatic potential of an ideal, infinite graphene sheet. Furthermore, the electrostatic potential should be negligible near the center of graphene samples with radii in the realm of hundreds of nanometers to a micrometer. These observations have led the authors of prior studies to neglect the atomic quadrupole of carbon in molecular dynamics simulations of graphene.\(^{167–169}\) Naturally, this begs the question what exactly did the W&B experiment measure? In any real, finite sample the net quadrupole moment will have a contribution from the atomic quadrupole moments of the interior carbon atoms as well a contribution from edge effects. Rearrangement of bonding, chemisorption, and adsorption can all take place at the edge carbon atoms to satisfy dangling bonds introducing edge dipoles into the electrostatics. W&B were aware that edge dipoles could play a role, but they had no way of eliminating this contribution. As such, they assumed that the net quadrupole moment

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of their sample derived from the atomic quadrupole of the carbon atoms rather than from edge effects. In doing so, W&B’s measurement of the bulk quadrupole was contaminated by edge dipoles along with the atomic quadrupole of carbon, $Q_{20}^C$.

While the BS-ISA calculations on the PAHs suggest that $Q_{20}^C$ of a carbon atom of graphene is very small in magnitude, one might expect that one could establish this definitively from an electronic structure calculation on graphene using periodic boundary conditions. The idea here being to calculate the quadrupole moment of the two-carbon atom unit cell and then dividing by two to obtain a value of $Q_{20}^C$. However, due to the use of periodic boundary conditions, only the primitive $Q_{20}$ moment, $\langle zz \rangle$, can be uniquely determined from such a calculation, and the $\langle yy \rangle$ and $\langle xx \rangle$ components become origin dependent. In spite of this limitation, it is instructive to calculate $\langle zz \rangle$ for the graphene sheet. To accomplish this, we have carried out DFT calculations on graphene with periodic boundary conditions, employing a two-atom cell with up to 16Å of separation between the graphene layers in the aperiodic direction. The Castep code was used, and the LDA, PW91, PBE, and PBE0 functionals were tested. Additional details on the calculations are provided in the supporting information document. All tested functionals yielded primitive quadrupoles within $-3.922 \leq \langle zz^a \rangle \leq -3.951$ a.u. and PBE0 with a norm-conserving pseudopotential yielded $\langle zz^a \rangle = -3.931$. These values are close to the $-4.03$ a.u. value of $\langle zz^a \rangle$ determined using the BS-ISA procedure for the C atoms of the central ring of dicircumcoronene. The primitive, $\langle zz^a \rangle$, and traceless, $Q_{zz}^C$, atomic quadrupole components are related as follows: $\langle zz^a \rangle = (2Q_{20}^a + \langle (r^a)^2 \rangle)/3$, where $\langle \ldots \rangle$ refers to a spherical average and $\langle (r^a)^2 \rangle = \langle (x^a)^2 \rangle + \langle (y^a)^2 \rangle + \langle (z^a)^2 \rangle$. Unfortunately, the mixed real space plus basis space approach used by the GDMA algorithm to partition the atomic domains makes it difficult to extract $\langle (r^a)^2 \rangle$. However, given the GDMA value of $Q_{zz}^C$ determined from the calculations on the PAHs, the associated value of $\langle (r^a)^2 \rangle$ would have to be $\sim -9.45$ a.u. to give a $\langle zz^a \rangle$ value consistent with the result of the PBC calculations on graphene. Again, this implies that GDMA yields a much more anisotropic charge distribution around the carbon atoms than does BS-ISA. We note that the tendency of GDMA to predict anisotropic atomic charge distributions was pointed out previously by Lillestolen and Wheatley.

In our discussion of the W&B determination of $Q_{20}^C$ of graphite, we highlighted the problem posed by edge dipoles. While this is a non-issue for idealized, infinite graphene sheets, experimental samples are necessarily finite and will contain edge effects, the impact of which should not be
neglected. To illustrate this further, we constructed two simple electrostatic models where we include or ignore edge effects. We model the electrostatics of graphene nanoflakes ($C_{6n^2}$; $n = 2, 3, \ldots$) using geometries that are identical to the PAHs we’ve considered thus far except that the hydrogen atoms have been removed. The effects introduced by hydrogen atoms are represented by model edge dipoles ($Q_{1m}^\text{CH}$). Whether the edge dipoles are present or absent from the model, we apply $Q_{20}^C$ to every carbon atom in the nanoflake. For the $C_{24}$, $C_{54}$, and $C_{96}$ nanoflakes we use the values of $Q_{20}^C$ tabulated in Table 4, and for nanoflakes larger than $C_{96}$ we use the $Q_{20}^C$ value of $C_{96}H_{24}$ as this quantity has converged with respect to system size and should change little for larger nanoflakes (again refer to Table 4). When edge effects are included, we apply a dipole of the same magnitude to every edge carbon atom that would have a hydrogen bound to it in the corresponding PAH. The edge dipoles were determined using a fitting procedure detailed in the supporting information document. Figure 16 shows the electrostatic interaction of a negative point charge with increasingly large carbon nanoflakes represented via our two electrostatic models.
Figure 16: The electrostatic interaction of a negative point charge with increasingly large carbon nanoflakes at a distance of 3.4 Å above the plane of the molecule. Results shown for only atomic quadrupole moments ($Q_{20}^{C}$) on the carbon atoms as well as those with dipoles ($Q_{1m}^{CH}$) on the edge carbon atoms. The x-axis in the figure, $r$, is an average distance of the edge carbons to the center of mass in the carbon nanoflake.

As seen from the figure, the contribution of the atomic quadrupoles is essentially negligible over the entire range of nanoflakes considered. On the other hand, the contribution of the edge dipoles to the electrostatics is orders of magnitude larger, being $\sim 3.1$ kJ/mol for the largest system considered (15000 C atoms) with a radius of about 111.5 Å. Although the graphitic nanoflakes considered by W&B had a much larger radius than those considered here and their samples included contributions from multiple graphene layers, the above analysis illustrates how edge effects can dominate the net electrostatic interaction.

In this article, we presented results that show that GDMA and BS-ISA give very different values of the atomic multipole moments of PAHs, with the GDMA results being consistent with the molecular quadrupole moment being dominated by the atomic quadrupoles of the C atoms and the BS-ISA results being consistent with the molecule quadrupole being dominated by edge dipoles. Significantly, the BS-ISA calculations give a primitive $Q_{20}^{C}$ value, $\langle zz'' \rangle$, very close to
that calculated for graphene via periodic boundary conditions. This is an important observation as $\langle zz'\rangle$ does not depend on a partitioning of the charge density. We further conclude that the $-0.675$ a.u. value of $Q_{20}^C$ reported by W&B for graphite may derive predominantly from edge dipoles. The present analysis demonstrates that even for graphene nanoflakes containing 15000 C atoms, there can be a sizable contribution to the electrostatic potential near the center of the ring due to dipoles at the edges of the system. We acknowledge that the dissection of the net quadrupole moment of a PAH into a contribution from the $Q_{20}^C$ moments and a contribution from the edge dipoles is not unique and cannot be established experimentally. Nonetheless, based on the accuracy and rapid convergence of the BS-ISA multipole expansion, we believe that it provides a more useful description of electrostatics than the GDMA procedure. Although our focus has been on hexagonal PAHs our conclusions are also relevant for graphene nanoflakes with edge terminations other than CH groups. With the above in mind, we assert that for flat graphene nanoflakes, the atomic quadrupole of carbon is immaterial for intermediate to long-range intermolecular interactions and more realistic force field simulations incorporate the relevant effects of edge termination into electrostatics.

4.3 Acknowledgements

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4.4 Supporting Information

Details describing the methodology used for obtaining multipole moments from BS-ISA, GDMA, and periodic boundary condition calculations, the evaluation of electrostatic interaction and charge penetration scans, and the process for constructing or model edge dipoles are available in the supplementary information document attached in appendix B.

4.5 Data Availability Statement

The data underlying this study, including but not limited to geometries, example inputs and outputs, plotting scripts, are openly available in the repository graphenes_quadrupole at https://github.com/dev-m-mulvey/graphenes_quadrupole.git.
5.0 Application of a Fluctuating Charge Polarization Model to Large Polyaromatic Hydrocarbons and Graphene Nanoflakes

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5.1 Summary

We present a polarization model incorporating coupled fluctuating charges and point inducible dipoles which is able to accurately describe the dipole polarizabilities of small hydrocarbons and, for sufficiently large graphene nanoflakes, reproduce the classical image potential of an infinite conducting sheet. When our fluctuating charge model is applied to the hexagonal carbon nanoflake \( C_{60000} \) we attain excellent agreement with the image potential and induced charge distribution of a conducting sheet and with the inclusion of inducible dipole terms, the model predicts an image plane of \( z_{\text{im}} = 1.3334 \, a_0 \), which falls in line with prior estimates for graphene. We consider the case of two charges placed on opposite sides of \( C_{60000} \) and find that the fluctuating charge model reproduces classical electrostatics once again. By testing opposing and like signs of the external charges, we conclude that an atomically thin molecule or extended system does not fully screen their interaction.

5.2 Main Body

The explicit inclusion of polarization in force fields is essential for accurate description of intermolecular interactions and adsorption of atoms and molecules at interfaces, particularly when the species interacting with the interface are charged or highly polar. Inclusion of polarization is
also essential in model Hamiltonian approaches to non-valence anions of molecules and molecular clusters.\textsuperscript{14,29,98,102,116} Most polarizable force fields treat only local polarization, most commonly through point inducible dipoles\textsuperscript{30,83–89} or Drude oscillators (sometimes referred to charge-on-spring models).\textsuperscript{84,175–177} Such force fields neglect long-range charge delocalization, which becomes increasingly important for molecules with shrinking HOMO-LUMO gaps.

One of the most common approaches to treating charge delocalization is through fluctuating charge (FQ) models\textsuperscript{71,72} based in the concepts of electronegativity equalization\textsuperscript{178} and chemical potential equalization.\textsuperscript{179,180} There are a variety of implementations addressing the shortcomings of the original FQ models,\textsuperscript{76–82} which will be discussed later on. There are models that combine both the local polarization of inducible dipoles with the long-range charge delocalization of FQ\textsuperscript{69,70,73,74} and we have recently shown\textsuperscript{181} that a modified version of the inducible charge-dipole model of Mayer-Åstrand model (MÅ),\textsuperscript{69,70} hereafter referred to as MMÅ1, closely reproduces the PBE0\textsuperscript{33–36} and MP2\textsuperscript{109} values of the dipole polarizabilities of hexagonal polyaromatic hydrocarbons (PAHs) belonging to the series $C_{6n^2}H_{6n}$ ($n = 1, 2, 3, \ldots$). The largest species that we were able to treat with density fitted (DF) PBE0 and MP2 methods were $C_{294}H_{42}$ and $C_{96}H_{24}$ respectively in ref.,\textsuperscript{181} in which the def2-TZVPD basis set,\textsuperscript{131,132} its Coulomb-exchange (JK),\textsuperscript{132} and resolution of identity (RI)\textsuperscript{133} fitting basis sets were employed. By adopting a trimmed version of the def2-SVPD basis set,\textsuperscript{131,132} along with its JK\textsuperscript{132} and RI\textsuperscript{133} fitting basis sets, we have been able to extend the data set to $C_{384}H_{48}$ and $C_{150}H_{30}$, at the density fitted PBE0 and MP2 levels, respectively. The trimmed def2-SVPD basis set removes the tight d function from the basis for C and the p functions from the basis for H. A finite field perturbative approach was employed in the program Psi4 v1.4a2\textsuperscript{129,130} to obtain the polarizabilities of the PAHs, the details of which are described in the repository containing all data reported in this study. The polarizability values calculated with the trimmed def2-SVPD basis set are slightly smaller ($\leq 6\%$) than those calculated with the larger basis set used in ref.,\textsuperscript{181} We report the values of the in-plane polarizability obtained with this smaller basis set along with the results of the MMÅ1 model in figure 17.
Figure 17: In-plane polarizabilities of hexagonal PAHs up to C_{384}H_{48}. Results are reported for the PBE0 and MP2 methods using a trimmed version of the def2-SVPD basis set as well as for the MMÅ1 model. The x-axis label $N_C$ denotes the number of carbon atoms in the PAH.

As seen from figure 17, the MP2, PBE0, and MMÅ1 values of the polarizability are in close agreement (within 3%). Ref.\textsuperscript{181} also reported polarizabilities obtained using the point inducible dipoles only and charge flow terms only in the MMÅ1 model. Those calculations revealed that the contribution from the point inducible dipoles to the in-plane component of the polarizability grows essentially linearly with molecule size, while that due to the charge flow terms grows approximately quadratically with system size. The net values of the in-plane polarizabilities are smaller than the sum of the induced dipole and charge flow terms calculated separately due to the cross term between these two contributions. Although not reported in figure 17, we note that the MP2, PBE0, and MMÅ1 models all give similar values of the out-of-plane polarizability, and that this component grows approximately linearly with system size.

The success of a FQ model in describing the polarizabilities of the hexagonal PAHs is surprising, as it is well known that such models tend to overestimate long-range charge transfer.\textsuperscript{76–81} This raises the following questions: Is the overestimation of long-range charge transfer more problematic in
larger PAHs? Or is the “issue” of overpolarization in FQ models actually moot due to the shrinking HOMO/LUMO gap and concomitant increase in metallic character with increasing size of the PAHs? Indeed, the documented problems of FQ models, overpolarization and exaggerated charge flow between atoms separated by large distances, arise when applied to molecular systems with insulating behavior.\textsuperscript{76,77,81} In this work, we address these questions by examining how closely the polarization potential between a point charge ($Q$) and large hexagonal carbon nanoflakes belonging to the series $\text{C}_{6n^2}$ ($n = 1, 2, 3, \ldots$) calculated with the MMÅ\textsubscript{1} model approaches the classical image potential, $-Q^2/(4|z|)$ (in atomic units), where the molecule is taken to be in the $xy$ plane. The absolute value of $z$ is used because the systems considered are isolated from a substrate and are symmetric with respect to reflection through the $xy$ plane. We also compare the induced charge distributions obtained from our model with those for an infinite, conducting sheet.

The polarization energy ($E_{\text{pol}}$) expression in the MÅ model is given by,

$$E_{\text{pol}} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} q_i T_{i-q}^{i,j} q_j - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} p_i \cdot T_{p-p}^{i,j} p_j$$

\hspace{1cm} - \sum_{i=1}^{N} \sum_{j=1}^{N} p_i \cdot T_{p-q}^{i,j} q_j + \sum_{i=1}^{N} q_i (\chi_i + V_i) - \sum_{i=1}^{N} p_i \cdot E_i$$

(62)

where $q_i$ refers to the induced charge, $p_i$ the induced dipole, and $\chi_i$ the atomic electronegativity of atom $i$. The quantities $V_i$ and $E_i$ represent, respectively, the value of an external potential and electric field at atom $i$ and $N$ is the number of atomic sites. In the present study we are not concerned with permanent charges on atoms, so terms coupling atomic electronegativities $\chi_i$ to induced charges (fourth sum in 62) do not contribute to the polarization energy. The $T_{i,j}$ and $T_{p-j}$ factors represent dampened electrostatic interaction functions between the induced multipoles. These functions are derived with the assumption that the atomic charge distributions are well described by Gaussian functions. Of special interest are the $T_{q-q}$ factors, defined as,

$$T^{i,j}_{q-q} \left[R^{i,j}_{q-q}\right] = \frac{\text{erf} \left( \frac{r_{i,j}}{R^{i,j}_{q-q}} \right)}{r_{i,j}}$$

(63)

where $r_{i,j}$ is an interatomic distance and $R^{i,j}_{q-q} = \sqrt{(R_{q_i}^i)^2 + (R_{q_j}^j)^2}$. The free parameters, $R_{q_i}^i$ and $R_{q_j}^j$, are the radii of the charge distributions of atoms $i$ and $j$, respectively. When $i = j$ and $r_{i,j} \to 0$, $T^{i,i}_{q-q}$ determines the atomic hardness, which is associated with the self-energy required to assemble the
isolated atomic charge distribution. Likewise, the self-energy required to assemble an isolated atomic induced dipole is obtained from the terms involving $T_{p-p}^{i,j}$ when $r_{i,j} \to 0$. The charge-charge ($T_{q-q}^{i,j}$), charge-dipole/dipole-charge ($T_{p-q}^{i,j}$), and dipole-dipole ($T_{p-p}^{i,j}$) expressions for damping interactions between induced moments on separate atoms and the corresponding self-energy expressions when $r_{i,j} \to 0$ are explained in detail in the works of Mayer and Åstrand.$^{69,70}$

The primary difference between the original MÅ and MMÅ1 models is in the choice of $R_q$ for a carbon atom which was increased from 0.0303 $a_0$ (MÅ) to 0.2365 $a_0$ (MMÅ1). This change was essential for obtaining dipole polarizabilities in good agreement with the PBE0 and MP2 results for the hexagonal PAHs considered in ref.$^{181}$ It is important to note that for both the MÅ and MMÅ1 models, the resulting $R_{q-q}^{i,j}$ values provide essentially no attenuation to the Coulomb interaction of charges between different atomic sites, even in the case of directly bonded carbon atoms. Other differences between the original MÅ model and the MMÅ1 model involve small adjustments in the atomic dipole polarizabilities and a modification of the damping of the charge-dipole and dipole-dipole interaction terms. The details are given in ref.$^{181}$
Figure 18: Polarization potential of a negative point charge ($Q = -1$) interacting with increasingly large hexagonal carbon nanoflakes calculated using the charge flow term of the MMÅ1 and MMÅ2 model. Results are shown the cases where the nanoflakes are constrained to have (a) a total charge of $Q_{\text{mol}} = 0$ and (b) a total charge of $Q_{\text{mol}} = 1$ using the MMÅ1 model. In (c) the MMÅ1 and MMÅ2 model are compared using a grounded ($Q_{\text{mol}} = 1$) C$_{60000}$ nanoflake. In all images, comparison is made with the classical image potential for a conducting sheet, $-1/(4|z|)$ in a.u.

Figures 18a and 18b report the polarization potentials calculated using the MMÅ1 model, retaining the charge flow terms only, for a unit point charge located from 5 to 10 $a_0$ above the plane of atoms along the principal rotational axis of hexagonal carbon nanoflakes: C$_{150}$, C$_{600}$, C$_{2400}$, C$_{15000}$, and C$_{60000}$. Obviously, the electronic properties of graphene nanoflakes depend on edge termination. In the context of the MMÅ1 model, the polarization potentials along the principal rotational axes are little affected by the removal of the H atoms, so these calculations can be viewed as being appropriate for hexagonal PAHs, C$_{6n}$H$_{6n}$, which can be viewed as H-terminated graphene nanoflakes. The figure also includes the $-1/(4|z|)$ potential from classical image potential theory (note that the figures report the potentials in eV).

The classical image potential is derived for a grounded sheet, which means that a negative unit charge above the surface induces a +1 charge on the surface. However, the same potential is expected for the ungrounded sheet since the induced charge can be “harvested” from infinite distances. In reporting results for the MMÅ1 model we considered both the grounded (net charge =
and ungrounded (net charge = 0) limits. We recognize that an induced charge equal in magnitude, but opposite in sign, from the interacting point charge for a finite “grounded” graphene nanoparticle or PAH is unphysical for a non-zero HOMO/LUMO gap, but should be physical in the limit of a zero gap. We also note that comparison with the classical image potential only makes sense for \( z \) values much less that the radius of the finite system considered.\(^{182}\) By limiting \( z \) values to 5 to 10 \( a_0 \), this condition is satisfied for all the systems reported in the figure except \( C_{150} \).

As seen from figure 18a, for the ungrounded nanoflake, the convergence of the polarization potential with increasing system size is very slow, with significant differences between the potentials for \( C_{15000} \) and \( C_{60000} \). The polarization potential from the charge flow portion of the MMÅ1 model for \( C_{60000} \) is less attractive than \(-1/(4|z|)\) with the difference being as much as 11% over the range of separations considered. The results for the nanoflakes constrained to have a charge of +1 are shown in figure 18b, from which it is seen that the convergence of the potential calculated using the MMÅ1 model with system size is much more rapid for the grounded case than the ungrounded case. Indeed, when \( Q_{\text{mol}} \) is constrained to be +1, the potential for \( C_{600} \) is close to that of \( C_{60000} \). However, even for \( C_{60000} \) the potential from the MMÅ1 model is up to 7.3% smaller in magnitude than the image potential result of \(-1/(4|z|)\). This suggests a limitation in the parameterization of the MMÅ1 model.

In considering factors that could cause the discrepancy between the polarization potential of \( C_{60000} \), as described by the MMÅ1 model, from the \(-1/(4|z|)\) image potential result, it occurred to us that this may be a consequence of the model having essentially no damping of charge-charge interactions. To explore this possibility, we multiplied the \( T_{i,j}^{\alpha} \) (where \( i \neq j \)) terms by a factor of \( 1 - e^{-\alpha r_{ij}} \), while keeping all other parameters of the MMÅ1 model fixed.

As seen in figure 18c, with the inclusion of the damping factor, with \( \alpha = 0.4191 \), the charge flow term in the modified MÅ model gives a polarization potential for \( C_{60000} \) which is essentially identical to that from the classical image potential when the nanoflake is assumed to be grounded. Hereafter, we refer to the model with additional charge-charge damping as MMÅ2. With the net charge of the nanoflake constrained to be zero, the MMÅ2 model gives a polarization potential for \( C_{60000} \) only about 4% less attractive than the image potential result. Presumably, this reflects the need to use an even larger nanoflake to converge the potential from the MMÅ2 model to the image potential result when the nanoflake is constrained to be charge neutral. The inclusion of the
damping factor leads to a moderate ($\leq 9\%$) increase of the in-plane polarizabilities of the hexagonal PAHs up to C$_{384}H_{48}$ in size compared to the PBE0 and MP2 results. While this could be remedied by making $R_q$ size dependent, changing with the HOMO-LUMO gap of the system, we have chosen instead to leave $R_q$ unchanged.

Another way of assessing the performance of the MMÅ2 model for describing the polarization of large hexagonal nanoflakes is to examine the charge distributions induced by a point charge above the plane of the molecule. In this context, we compare the charge distributions induced by a point charge interacting with the C$_{60000}$ nanoflake as described by the charge flow contribution of the MMÅ2 model and a grounded, conducting slab. In the case of the nanoflake, the point charge is located on the main rotational axis, while for the slab it is located at $(0,0,z)$. The expression for the induced charge density at the surface of a grounded slab induced by a point charge $Q$ at $(0,0,z)$ is given by,

$$\rho(r) = -Q \left[ \frac{z}{(z^2 + r^2)^{\frac{3}{2}}} \right]$$ (64)

where $r$ is the radial distance in the plane of the surface measured from the origin ($r = \sqrt{x^2 + y^2}$) and $Q$ is value of the external charge. This expression makes use of polar coordinates and includes the integration over the angle $\phi$ from 0 to $2\pi$. One can obtain the cumulative charge enclosed within a finite radius $R$ by integrating equation 64 from the origin up to $R$, which gives:

$$q_{\text{cumulative}}(R) = -Q \left[ 1 - \frac{z}{(z^2 + R^2)^{\frac{1}{2}}} \right]$$ (65)

Figure 19 reports the cumulative charge distributions for the C$_{60000}$ nanoflake interacting with a negative unit charge at (0,0,5) and (0,0,10) a$_0$, figures 19a and 19b respectively, as described by the MMÅ2 model with net induced charge constrained to be either +1 or 0. The corresponding charge distributions given by equation 65 are also reported. To obtain the results for the MMÅ2 model we sum the charges of all C atoms within radius $R$. 

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Figure 19: Cumulative charge of a C\textsubscript{60000} nanoflake induced by a point charge (Q = −1) at (0, 0, z) as described by the charge flow contribution of the MMA\textregistered 2 model when the nanoflake is grounded (Q\textsubscript{mol} = +1) or ungrounded (Q\textsubscript{mol} = 0). The cumulative charge for a thin, conducting slab is included for comparison. The cumulative charge is plotted with respect to the radial distance from the center of the carbon sheet. Two cases are considered: (a) the negative point charge is 5 and (b) 10 a\textsubscript{0} above the molecular plane along the principal rotation axis.

Overall, there is good agreement between the charge distributions from the FQ model (with a net molecular charge of +1) and that from the classical treatment of a grounded metallic sheet. When the net induced charge is constrained to be zero, the charge distribution of C\textsubscript{60000} induced by the point charge and calculated using the MMA\textregistered 2 model closely follows that of Eq 4 up to about R = 80 a\textsubscript{0}, after which the induced charge switches sign. It is important to note that the change of sign in the induced charge for large R values proves relatively unimportant to the electrostatic potential above (or below) the middle of a nanoflake with 60,000 atoms provided z is much smaller than the molecular radius. This is because the interactions between the external charge and induced atomic charges at short to intermediate range dominate the electrostatics near the central ring when z \ll R.
The results presented above demonstrate that the overestimation of long-range charge transfer is not a major problem when the MMÅ2 model is applied to large hexagonal PAHs or carbon nanoflakes. We believe that there are two factors that act to prevent the breakdown of the model:

1. The increasing metallic behavior as one progresses to larger systems.
2. The repulsive interactions between the induced charges on C atoms near the periphery of the molecule.

It is well known that an improved description of the polarization potential resulting from a point charge interacting with a conducting sheet includes a shift in the “image plane” which accounts for the displacement of the charge distribution outside the plane of atoms. This image plane shift results in a \(-\frac{Q^2}{(4|z - \text{sgn}(z) \ast z_{im}|)}\) potential, where \(z_{im}\) gives the location of the image plane and \(\text{sgn}(z)\) is included to reflect the fact that the systems of interest are isolated and are symmetric with respect to reflection in the \(xy\) plane. In a recent study a value of \(z_{im} = 1.98 \ \text{a}_0\) was deduced for the image plane of graphene. Obviously, a FQ model allowing only in-plane charge redistribution cannot account for the image plane shift. However, the full MMÅ2 model including both point inducible dipoles and charge flow terms can partially account for this effect. This can be seen in figure 20 which compares the polarization potential for \(C_{60000}\) from the full MMÅ2 model to \(-\frac{1}{(4|z - 1.98|)}\).
Figure 20: Polarization potential due to a negative point charge \( (Q = -1) \) interacting with a grounded \( (Q_{\text{mol}} = +1) \) C\textsubscript{60000} nanoflake as described by the full MMÅ2 model with both charge flow and inducible dipoles. The shifted-plane classical image potential is included for reference with the image plane parameter set to \( z_{\text{im}} = 1.98 \) a\textsubscript{0}, as determined in ref.\textsuperscript{28} A fit of the polarization potential from the MMÅ2 model to a function of the form \(-6.8028/|z - b|\), where \( b \) is a free parameter, is reported.

Overall, there is fairly good agreement between the two potentials, although that from the MMÅ2 model is less attractive than the shifted image plane result, with the difference being as large as 16\% at \( z = 5 \) a\textsubscript{0}. While this could reflect a deficiency in the inducible atomic dipoles of the MMÅ2 model, we note that if \( z_{\text{im}} \) is reduced to 1.3334 a\textsubscript{0}, the polarization potential from the MMÅ2 model and the shifted-plane image potential would be in excellent agreement. This can be seen in the curve fit to the MMÅ2 data in figure 20. Values of \( z_{\text{im}} \) as small as 1 a\textsubscript{0} have been considered in the literature.\textsuperscript{185}

There has been considerable debate in the literature\textsuperscript{186–191} as to whether a single layer of graphene is fully screening, i.e., whether a graphene sheet fully screens out the interactions of molecules on one side of a graphene surface from molecules or a solid substrate on the other side of
the sheet. Much of this debate has centered around whether a substrate, in the absence of charge transfer between the substrate and the graphene layer, impacts the contact angle of a water droplet on the other surface. If graphene were realistically described as a thin conducting slab, then the net interaction energy of two point charges \( Q \) at distances \( z \) and \( -z \) from the sheet would be \( -Q^2/(2|z|) \), independent of whether the charges are of the same or of different sign. This is simply the sum in the interactions of the point charge on each side with its induced charge distribution.

In figure 21 we report the net energy of the \( C_{60000} \) system with two point charges of -1 on opposite sides of the sheet (at \( z \) and \( -z \)) as described by the MMÅ2 model, retaining only the charge flow terms. Note that the net charge of the nanoflake is constrained to be +2.

![Figure 21: Total interaction of two negative point charges on opposing sides of a grounded (\( Q_{\text{mol}} = +2 \)) \( C_{60000} \) nanoflake as described via the charge flow contribution of the MMÅ2 model. The classical image potential solution for an intervening conducting sheet, \(-1/(2|z|)\) (a.u.), is included for reference. A fit of the model potential to a function of the form \( A/|z| \), where \( A \) is a free parameter, is included.](image.png)

The net interaction energy for this system obtained using the charge flow component of the MMÅ2 model is nearly identical to \(-1/(2|z|)\), the classical image potential result. However, in the MMÅ2 model the two point charges induce a cumulative charge redistribution in the plane of the
atomic sites in contrast to the classical result for a conducting sheet, where each point charge induces a separate charge redistribution in the surface it faces. If the two point charges are of opposite sign, the net interaction energy for a conducting sheet is still \( -1/(2|z|) \). Although the MMÅ2 model also reproduces this result, the “physics” is quite different. In the charge flow contribution of the MMÅ2 model, there is no induced charge when the two point charges are of opposite sign, and one simply has the interaction between the two point charges. In the conducting slab model, the point charge on each side of the sheet induces a charge distribution of opposite sign on the side that it faces. These external charge-induced charge distribution interactions screen the direct interaction between the two external point charges. While one might conclude that the MMÅ2 model is getting the “right answer for the wrong reason” we believe that it actually provides a more realistic description of charge flow polarization in graphene and in large hexagonal carbon nanoflakes than does the conducting slab model. In other words, we believe that an atomically thin molecule or extended system does not fully screen interactions between charges on its opposite faces.

Although not shown in this manuscript, we also calculated for a C_{15000} nanoflake the polarization energy resulting from the interaction of two point charges of like and opposite sign when point inducible charges and dipoles are included in the MMA2 model. When the external charges are of opposite sign (\( \pm 1 \)), the polarization of the nanoflake energy is entirely due to the \( z \)-component of the inducible dipoles. This energetic contribution is smaller than the Coulomb attraction between the external point charges and is approximately proportional to \( z^{-2} \). In contrast, when the two point charges are of the same sign, the contribution from the inducible dipoles originates from the in-plane components (\( x \) and \( y \)) only. This energetic contribution is small relative to both the Coulomb repulsion between the external charges and the attraction between the external and induced charges.

In this work we have shown that a modified Mayer-Åstrand model (denoted MMÅ2) including both point inducible dipoles and fluctuating charge polarization terms is able to accurately describe the dipole polarizabilities of small PAHs and, for sufficiently large graphene nanoflakes, reproduces the classical image potential for a conducting sheet. To our knowledge, this is the first application of coupled fluctuating charges and inducible dipoles in modeling the behavior of large carbon nanoflakes. We have demonstrated that the polarization behavior of extended systems, like graphene, can be modeled via large finite analogues. The MMÅ2 model is expected to be well suited in
describing polarization interactions in the adsorption of ions and molecules on large PAHs, graphene nanoflakes, and graphene itself. In the near future, we plan on applying this polarization model to study the non-valence anionic states of these finite nanoflake systems with the hope of demonstrating their connection to the image potential bound states of graphene.

5.3 Acknowledgements

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5.4 Data Availability Statement

The data underlying this study are openly available in the following repository https://github.com/dev-m-mulvey/CE_polarization_of_large_nanoflakes.git.
6.0 Demonstrating the Connection Between Non-valence Correlation-bound Anions and Image Potential States using a One-Electron Model Hamiltonian

This work is in preparation and has not been submitted to a journal as of yet.

6.1 Summary

We present results establishing that with increasing system size, the non-valence correlation bound (NVCB) anions of the polycyclic aromatic hydrocarbons (PAHs) \( C_{6n^2}H_{6n} \) and of carbon nanoflakes (CNs) \( C_{6n^2} \) evolve into the image potential states (IPSs) of graphene. The ground and excited state NVCB anions of PAHs are characterized using a one-electron model Hamiltonian, which incorporates atomic electrostatic moments up to the quadrupole, coupled inducible charges and dipoles, and atom-centered repulsive Gaussians to describe the interaction between the excess electron and PAH. We observe a variety of NVCB anions for select PAHs within the range \( C_{6n^2}H_{6n} \ n = 3 \) to 30. NVCB anions with nodes normal to the carbon atom plane are observed only for PAHs with 600 or more carbon atoms. Extrapolation of the electron binding energies (EBEs) of the lowest energy NVCB anions predicted for these PAHs to the limit of an infinite graphene sheet yields binding energies that agree reasonably well with past periodic boundary condition (PBC) calculations\(^{27,28}\) and two-photon photoemission spectroscopy (2PPE) experiments\(^{192,193}\).

6.2 Introduction

Non-valence correlation bound (NVCB) anions constitute a class of stable anions that are markedly different than their valence counterparts. While short-range interactions stabilize valence anions, it is long-range, “dispersion-like,” correlation that stabilizes NVCB anions. This correlation constitutes configurations in which the excess electron and valence electrons of the neutral molecule are both excited. The Hartree-Fock (HF)\(^{106–108}\) method and many post-HF methods will fail to bind
NVCB anions, as it is essential to include electronic configurations that allow the orbital occupied by the excess electron to, “relax,” in response to dispersion-type correlation.\textsuperscript{16,25} Theoretical studies have predicted\textsuperscript{1,9,12,14–16,23–25,29,98–103,181} and experimental studies have suggested or confirmed the existence of NVCB anions for a variety of molecules and molecular clusters.\textsuperscript{4,6–8,104,105,194}

Near the maximum conduction band (or analogously highest energy virtual orbitals) of a metal or semiconductor there is an infinite set of electronic states, dubbed image potential states (IPSs), that extend to up to the vacuum level (the continuum of unbound free electron states). In these states, the excess electron is bound at long-range by a non-local self-induced image potential which derives from the collective polarization response of the conductor’s electrons to the presence of the excess electron.\textsuperscript{183} It has been suggested that the NVCB anions and IPSs are related since in a many-body treatment, IPSs are bound by the same type of dispersion-like correlation that stabilizes NVCB anions.\textsuperscript{14–17} However, the connection between these diffuse anions, belonging to two different size regimes, has not been rigorously established. In a previous publication, we characterized the lowest energy NVCB anion of hexagonal polycyclic aromatic hydrocarbon (PAH)s $\text{C}_{6n^2}\text{H}_{6n}$ ($n = 3–7$) using a one-electron model Hamiltonian.\textsuperscript{181} In the present study we extend this work to larger PAHs and CNs with the goal of examining the evolution of the NVCB anions of these species to the IPSs of graphene.

The behavior of the image potential can be illustrated using a simple model from classical electrodynamics. Consider a point charge ($Q$) placed a distance $z$ above a grounded infinitely conducting plate and one wants determine the potential it experiences. Charge carriers at the conductor’s surface rearrange and using superposition the charge distribution is modeled via an effective image charge of the same magnitude, opposite in sign ($-Q$), which is situated on the other side of the conducting plane at $-z$. The attractive potential $Q$ experiences can be expressed as (in a.u.),

$$V(z) = -\frac{Q^2}{4z}$$  \hspace{1cm} (66)

The potential given by equation 66 is only valid in the positive half space above the conductor ($z > 0$), as it pertains to a conductor with infinite extent in the negative half space ($z < 0$). However, in the case of graphene where the system is atomically thin, the potential is valid in both half spaces, which is achieved by taking the absolute value of $z$ in equation 66. A common correction applied to equation 66 is to shift the denominator by a constant referred to as the, “image plane,” ($z_{im}$) like so,
\( V(z) = -Q^2/4(z - z_{im}) \). This correction reflects the fact that the surface of a metal or semiconductor does not terminate at the uppermost layer of nuclei, rather the electron density has some extent into the space above them.\(^{183}\)

If an excess electron is captured by the image potential of a metallic surface, theory predicts that it occupies a series of wavefunctions with the following energetic ordering:

\[
E_n^\pm = -\frac{0.85\text{eV}}{(n + a_n)^2} n = 1, 2, 3, \ldots
\]

(67)

Where 0.85 eV is 1/16th the Rydberg energy, \( n \) refers to the number of nodes in the wavefunction, and \( a_n \) is a quantum defect, which corrects the energy levels to account for the material’s band structure.\(^{26,195,196}\) Note that one-dimensional nature of this model means that image potential states (IPSs) are quantized in the \( z \)-direction (by way of the image potential), but the electron has complete freedom of movement in dimensions co-planar to the conductor (\( x \) and \( y \)).

In the case of a free-standing graphene sheet with no underlying substrate, an excess electron binds to both faces of the atomic plane and theory predicts that the coupling between the states belonging to either side yields a double series of antisymmetric \((n^- = 1^-, 2^-, 3^-, \ldots)\) and symmetric \((n^+ = 1^+, 2^+, 3^+, \ldots)\) IPSs. The parity of the roots are classified by whether they do (-) or do not (+) change sign when passing through the carbon atom plane and the quantum number \( n \) counts the number of nodes normal (in the \( z \)-direction) to the carbon atom plane, \textit{as a pair}. This means that the wavefunction of the first odd IPS, \( n = 1^- \), has a node above and below the carbon atom plane \((n = 1)\) and another node within the carbon atom plane (-). The wavefunction of the first even IPS, \( n = 1^+ \), has a node above and below the carbon atom plane \((n = 1)\), but it does not change sign at the carbon atom plane (+). In each energetic series a correction \((a_n^\pm)\) is applied to the energy levels to account for the electronic structure of graphene, with separate values existing for even \((a_n^+\) and odd \((a_n^-)\) states.\(^{27,28}\) Experimental evidence for the theoretically predicted double series is scant, but there are three independent studies that identified electronic states of a pseudo-free standing graphene sheet weakly coupled to a SiC substrate that they ascribed to the first even \((1^+)\) and odd \((1^-)\) IPSs.\(^{192,193,197}\) Another experimental study on graphene supported by SiC identified a single series \((n = 1, 2, 3, \ldots)\), not double series \((n^\pm = 1^\pm, 2^\pm, 3^\pm, \ldots)\), so there does not appear to be a clear consensus in the literature.\(^{198}\)
Some readers may recognize the direct connection between the above equations describing the bound surface states of metals and the controversial 1D hydrogen atom problem.\textsuperscript{199} We will not revisit the decades of literature addressing the theoretical pitfalls associated with the 1D hydrogen atom, but the interested reader will find the introduction and underlying references in the following publication enlightening.\textsuperscript{200} However, we do note that much of the fundamental issues associated with the 1D hydrogen atom are irrelevant for the physical systems under consideration. The problematic singularity in the image potential ($\lim_{z \to 0} V(z)$) appears where other short-range interactions dominate and this fact has been sufficiently addressed in prior ab initio and model calculations. In periodic boundary condition (PBC) treatments of the IPSs of graphene and solid beryllium, the authors replace the divergent portion of $V(z)$ with the short-range exchange-correlation potential of a local DFT method (e.g., LDA).\textsuperscript{26–28} Alternatively, De Andres et al. opted to represent graphene as an infinite polarizable dielectric via Thomas-Fermi theory and random phase approximation (RPA) in a one-dimensional one-electron model, which exhibits the correct $-1/4|z|$ asymptotic image tail and avoids the singularity ($\lim_{z \to 0} V(z)$) at short-range.\textsuperscript{185}

Setting aside the considerations regarding the simulation of an infinite graphene sheet, there are a separate set of effects that arise when one works with its finite analogs. Shrinking graphene down to the nanoscale introduces confinement in the two spatial dimensions belonging to the carbon atom plane, altering not only the occupied electron states but the unoccupied IPSs as well. To our knowledge, there are no experimental or theoretical studies of image potential-like states of isolated CNs and PAHs. Nearly all the relevant experimental studies of graphene’s nanoscale analogs have a supporting metal substrate, and study the how the carbon nanostructures modify the IPSs of the underlying metal substrate.\textsuperscript{119,201} The lack of experimental and theoretical data on the non-valence anions of large nanoflakes, makes it difficult to validate the NVCB states predicted by our gas phase simulations. However, by studying the NVCB anions of increasingly large PAHs we should be able to assess if the limiting behavior of our model produces IPS-like states with energetic ordering similar to equation 67. Furthermore, the ability to remove (CNs) or include (PAHs) model electrostatics enables us to assess the relative impact of model potential components on NVCB anion states.

There were limitations that prevented us from probing the NVCB anions of larger systems, namely a lack of reference data to evaluate the model’s performance, an electrostatic model
applicable to large PAHs, and a polarization model that asymptotically converges to the image potential. To address the above issues we invested effort into the electrostatic and polarization components of our one-electron model. We developed a minimal quadrupole+edge CH dipole electrostatic model for large PAHs, inaccessible to quantum mechanical methods, using atomic multipole data from basis space-iterated stockholder atoms (BS-ISA) calculations\(^{64}\) (see chapter 4). After introducing additional damping into the induced charge-induced charge interactions and refining the parameters of our polarization model, we were able to reproduce the classical image potential and induced charge distribution for an infinite conducting slab with large CNs like \(C_{6000}\)\(^{202}\) (see chapter 5). With these refinements in place we are able to push the model further probing the NVCB anion states of large PAHs.

In this work, we use our one-electron model to study the NVCB anions of PAHs ranging in size from tens to thousands of atoms. We characterize qualitative trends in the electron binding energies (EBEs) and single particle orbitals of these NVCB states like the relative impact of electrostatics and polarization. We aim to determine if there are NVCB states reminiscent of the first few IPSs of graphene. By extrapolating the EBEs of these select NVCB anions we will see if it is possible to reproduce the energetic series of graphene’s IPSs. We will probe confinement effects that are intrinsically present in experimental samples, but cannot be addressed in dielectric continuum models and PBC calculations.

\section{6.3 Methods}

The one-electron model employed in this work has been discussed at length in prior publications,\(^{12,14,29,181,202}\) so we will only review the pertinent details briefly. This work aims to solve the time-independent electronic Schrödinger equation for a single excess electron bound to carbon-based systems consisting of tens to thousands of atoms. To model the excess electron’s interaction with these molecules we employ a model Hamiltonian of the form,

\[
\hat{H}(\mathbf{r}) = \hat{T}(\mathbf{r}) + \hat{V}_{es}(\mathbf{r}) + \hat{V}_{pol}(\mathbf{r}) + \hat{V}_{rep}(\mathbf{r})
\]  

(68)
where $\hat{T}(\mathbf{r})$ is the kinetic energy operator for the excess electron and the operators $\hat{V}_{es}(\mathbf{r}), \hat{V}_{pol}(\mathbf{r})$, and $\hat{V}_{rep}(\mathbf{r})$ represent, respectively, the electrostatic, polarization, and repulsion potentials that the excess electron (positioned at $\mathbf{r}$) experiences in the presence of the molecule. The molecule’s charge distribution and its interaction with the excess electron is represented approximately via the classical model potentials in equation 68. When the operators in equation 68 act on the eigenvectors representing the excess electron, the terms $V_{es}(\mathbf{r}), V_{pol}(\mathbf{r})$, and $V_{rep}(\mathbf{r})$ provide the potential energy surface upon which the excess electron moves.

The molecule is treated as a fixed rigid body and the energy of the excess electron is evaluated on a real space grid of points, $\mathbf{r}$, using a sine-type discrete variable representation (DVR) basis. Both the molecule and excess electron are contained within a three-dimensional box where the potential is finite within the box and infinite outside of it. The construction of the sine DVR basis starts from particle in a three-dimensional box (3D-PIB) eigenfunctions. The space within the box is discretized into a grid of evenly spaced points, at which one constructs the sine-DVR basis functions of the excess electron by taking linear combinations of the 3D-PIB eigenfunctions. Due to the orthogonality of the PIB eigenfunctions and the applied quadrature rule, the sine-DVR basis functions behave like delta functions taking on a value of unity at the grid points they are centered on and a value of zero at every other grid point. As a result, the potential matrix is diagonal in this representation. The kinetic energy is not diagonal in the sine-DVR basis, but is given by relatively simple analytical expressions. For more details regarding the nature of the sine-DVR basis, see the following publications or chapter 3.

The classical model potentials used to represent the charge distributions of the PAHs have been discussed at length in the preceding chapters and their corresponding publications. To represent the static charge densities of the PAHs we use atomic charges, dipoles, and quadrupoles derived from distributed multipole expansion (DME) calculations. For smaller systems, which can be simulated via a quantum mechanical calculation, we use Gaussian distributed multipole analysis (GDMA) moments extracted from PBE0 densities as described by the cc-pVDZ basis set. For large PAHs inaccessible to quantum mechanical calculations we use the out-of-plane quadrupole ($Q_{20}$) and edge CH bond dipole model constructed from BS-ISA moments, which is described at length in chapter 4.

To model the polarization response of the PAHs to the excess electron we use an inducible
charge and dipole model adapted from the work of Mayer and Åstrand.\cite{69,70} For more details on the polarization model, one can refer to section 2.4 of chapter 2. The development of polarization model parameters for smaller PAHs are described in chapter 3\cite{181} and the details pertaining to large CNs and PAHs are described in chapter 5.\cite{202}

The short-range divergence of electrostatics and polarization is removed from the model potentials using an effective distance damping scheme described in chapter 3. This damping does not include short-range effects like the orthogonalization of the excess electron’s orbital to the occupied states of the neutral molecule, electrostatic charge penetration, and electronic exchange. All these missing effects are folded into the repulsive potential, which is modeled via spherical Gaussians on every atom. Once again, one can refer to chapter 3 to see the details of this potential.

### 6.4 Calculation Details

First, we revisit the small PAHs ($C_{6n}H_{6n}$ ($n = 3−7$)) we considered in a prior publication.\cite{181} For these PAHs we extracted 10 to 15 eigenpairs from the model Hamiltonian using the implicitly restarted Lanczos Arnoldi\cite{203} diagonalization routine implemented in ARPACK\cite{204} with a cutoff of $1 \times 10^{-5}$ on the eigenvalues’ residuals. The converged roots were passed to an in-house coded implementation of Davidson’s diagonalization\cite{205} routine with a looser cutoff of $1 \times 10^{-3}$ on the residuals. This second diagonalization was performed as a post processing step where the orthogonalization and a few matrix times vector iterations were performed on the converged Lanczos-Arnoldi eigenpairs to correct erroneous behavior in the energetic ordering and shape of single particle orbitals. Every PAH was placed in a square simulation box with a side length of 230 a.u. with a 1 a.u. spacing between DVR grid points. The charge distribution of the PAHs were modeled using the repulsive $s$ Gaussian parameters and PBE0/cc-pVDZ\cite{33–36,145} electrostatic atomic multipoles extracted for these molecules in our previous publication studying the lowest energy NVCB anion of these systems (see chapter 3).\cite{181} Two sets of calculations were performed for every PAH: one set uses the MMÅ1 inducible atomic charge and dipole model we developed for small PAHs in the aforementioned publication\cite{181} and the other uses the MMÅ2 inducible atomic charge and dipole model we developed for the polarization of large CNs and PAHs.\cite{202}
For the CNs ($C_{6n^2}$) and PAHs ($C_{6n^2}H_{6n}$) with indices $n = 10, 12, 15, 20, 25,$ and $30$ we use the same diagonalization routines and process for extracting eigenpairs described for the smaller systems. A total of fifteen eigenpairs were extracted for first four systems considered $n = 10, 12, 15,$ and $20$, twenty roots were extracted for $n = 25$, and twenty five roots were extracted for $n = 30$. The only exception to the above description is the number of eigenpairs calculated for $n = 30$ CN, $C_{5400}$, for which twenty roots were extracted. Various sizes of simulation boxes were tested and it was determined that a square simulation box with a side length of 400 a.u. is appropriate for all CNs and PAHs except $n = 25$ and $30$. A rectangular box with dimensions $L_x, L_y = 500$ and $L_z = 250$ a.u. was used for $n = 25$ and $30$. Computational limitations in the implementation of the Davidson diagonalization routine necessitated the use of a 2 a.u. DVR grid spacing for these larger systems. The MMÅ2 inducible atomic charge and dipole model was used for polarization. In simulating the CNs we neglect electrostatics and for PAHs we use the electrostatic model described in chapter 4. This model assigns an out-of-plane quadrupole component ($Q_{20} = -0.006$ a.u.) to every carbon atom and an atomic dipole to the edge carbon atoms bound to hydrogen. The atomic dipoles on edge carbon atoms model the CH bond dipoles, absorbing the contributions of atomic charges and dipoles on the carbon, hydrogen pair.

Last we note that the large CNs ($C_{6n^2}$) we consider in this work are hypothetical systems. The geometries of the CNs considered in this work are the same as the PAHs except they lack the hydrogen atoms terminating the $sp^2$ hybridized carbon atoms at the edges of the carbon atom plane. Experimentally synthesized CNs can come in a variety of shapes, sizes, and the edge terminations depending on the synthetic approach employed. It is possible to produce graphene samples and nanostructures terminated by carbon atoms, but they can undergo rearrangement or gaseous molecules may adsorb to satisfy the valencies of edge carbon atoms. The model binding energies and single particle orbitals extracted for the anions of these CN systems are used to assess the impact of electrostatics on the NVCB states of PAHs and they should not be considered predictive of what would be observed for physical CN samples.
6.5 Results & Discussion

In prior work, we studied the lowest energy NV-CB anions of hexagonal PAHs \( C_{6n}H_{6n} \) \((n = 3 - 7)\) in depth. A natural extension of that work is to extract the bound excited states to see how the one-electron model fairs. Figure 22 shows the single particle orbitals, the EBEs, and symmetries of the first few bound NV-CB states predicted by the one-electron model. The model potential components include charges and dipoles, repulsive Gaussians, and GDMA atomic electrostatic moments up to the quadrupole derived from PBE0/cc-pVDZ densities. The EBEs are evaluated with (MMÅ2) and without (MMÅ1) the exponential charge flow damping introduced in chapter 5.202

![Diagram of orbitals for various PAHs]

Figure 22: EBEs in meV and single particle orbitals for NV-CB anion states of the PAHs: \( C_{54}H_{18} \), \( C_{96}H_{24} \), \( C_{150}H_{30} \), \( C_{216}H_{36} \), and \( C_{294}H_{42} \). Binding energies are reported for both the MMÅ1 and (MMÅ2) polarization models, while the orbitals are from the calculations using the MMÅ1 polarization model. Orbitals are plotted at 90% charge enclosure of the excess electron’s density using VMD.134 The orbital labels are based on the hydrogenic orbitals that they resemble. Symmetry labels and EBEs for anions that are energetically degenerate (or nearly degenerate) are listed within the same row separated by a comma.

Before going forward we must address the issue of roots that should be doubly degenerate differing in their EBEs (e.g., 4\( f \)-like states for \( C_{216}H_{36} \) and \( C_{294}H_{42} \) in figure 22). Multiple tests
were run to probe this and the primary factors appear to be numerical in nature. The EBEs of states that should be degenerate tend to be sensitive to the number of roots requested and size of Hamiltonian subspace used during diagonalization. Increasing both of these parameters, corrected this undesirable behavior for the energetically lower lying states, but it persists for the highly excited anionic states. The diagonalization routines employed are not robust enough to push to very large subspaces, but we are exploring alternative implementations and math libraries. This problem would likely resolved by explicitly enforcing symmetry in the model potential and the kinetic energy Hamiltonian elements and using symmetry adapted DVR basis functions. Regardless, we are primarily interested in the first few anionic states which are tolerant to these numerical difficulties.

One can see in figure 22 that the only bound state for C$_{54}$H$_{18}$ is the 1$s$-like NVCB anion, while the larger PAHs support $p$-like and $d$-like excited state NVB anions, which happen to bear a strong resemblance to those predicted computationally and experimentally observed for fullerenes and fullerene clusters.$^{7,12,14,24,29}$ The calculations predict that none of these PAHs are capable of supporting an NVCB state with a node normal to the carbon atom plane (e.g., 2$p_z$, 3$d_{xz}$, 3$d_{yz}$, . . . ). This phenomena is the result of two factors: an energetic destabilization of excited states with nodes normal to the carbon atom plane and the edge localization driven by electrostatics (discussed at length in chapter 3$^{181}$). To test the latter assertion, we performed the same calculations for C$_{150}$H$_{30}$, C$_{216}$H$_{36}$, and C$_{294}$H$_{42}$ in the absence of model electrostatics and observe a 2$p_z$-like excited state for all three PAHs.

When the MMÅ1 polarization model is used, the EBE of the lowest energy 1$s$ state of C$_{54}$H$_{18}$, 12.3 meV, matches the EOM-MP2 results of Voora and Jordan.$^{15}$ This much was confirmed in our first study of the lowest energy NVCB anion of these PAHs (see chapter 3).$^{181}$ However, Voora$^{210}$ was able to extend the all-electron calculations further using the RPA, which is a class of methods that is growing more popular in the treatment of non-covalent interactions.$^{211–213}$ Using RPA, Voora was able to extract the ground and first excited NVB state of C$_{96}$H$_{24}$. These RPA calculations predict that the ground state NVB anion of C$_{96}$H$_{24}$ is 1$s$ and the first excited state is a planar 2$p$ state with EBEs of 85.6 and 40.8 meV respectively. These preliminary calculations lend credence to our model’s predicted $p$-like excited states. However, the RPA EBEs for C$_{96}$H$_{24}$ are likely too large. RPA calculations on C$_{54}$H$_{18}$ predict an 1$s$ ground state NVB anion with an EBE of 31.4 meV, which is appreciably larger than the EOM-MP2 value of 12.3 meV. This is further evidenced by
RPA predicting a weakly bound (∼1.9 meV) 1s state for C$_{24}$H$_{12}$, which is absent from our model predictions and prior EOM calculations by Voora and Jordan.$^{15}$

There are appreciable differences between the results obtained with the MMÅ2 and MMÅ1 inducible charge models, which are listed (inside) and outside the parentheses respectively in figure 22. For the 1s NVCB anion, the discrepancy between EBEs obtained using the MMÅ1 and MMÅ2 is not dramatic and it tends to decrease with system size dropping, from 38% for C$_{54}$H$_{18}$ to 17% for C$_{294}$H$_{42}$. The discrepancy in model EBEs is more pronounced for the excited states, with percent differences being as small as 17% and as large as 99%. However, these discrepancies tend to decrease with system size; in going from C$_{54}$H$_{18}$ to C$_{294}$H$_{42}$ the percent difference in MMÅ1 and MMÅ2 EBEs decrease from 45 to 17% for $p$-like states and 73 to 21% for $d$-like states. The larger binding energies produced by the MMÅ2 model are not unexpected, as the exponential damping added to the MMÅ1 model was tuned to reduce repulsion between induced charges and enhance the polarization energy such that it reproduces the image potential on large nanoflakes (see chapter 5).$^{202}$ This also explains why the differences in MMÅ1 and MMÅ2 EBEs tend to shrink with the size of the PAHs, as the polarization of these systems takes on a more metallic character.

While, MMÅ1 reproduces the EOM-MP2 1s ground state EBE of C$_{54}$H$_{18}$ calculated by Voora and Jordan, it has been shown that including higher-order electron correlation can increase NVCB binding energies appreciably. For example, Voora et al.$^{16}$ and Upadhyay et al.$^{25}$ have both shown that the difference between EOM-CCSD and EOM-CCSDT binding energies for the ground state NVCB anion of the (H$_2$O)$_4$ cluster can be as large as ∼ 10 to 30 meV depending on the molecular cluster’s geometry. It is likely that an EOM-CCSDT calculation would yield an EBE larger than that of Voora and Jordan’s EOM-MP2 estimate for C$_{54}$H$_{18}$. Thus, it is not obvious whether the MMÅ1 or MMÅ2 polarization model produces results that are more accurate.

What is clear is that as the size of these PAHs approach the nanoscale the MMÅ2 polarization model becomes more appropriate. This was demonstrated in our prior publication (chapter 5), where the exponential damping applied to induced charge interactions was crucial to our polarization model reproducing the image potential and concomitant induced charge density.$^{202}$ With this in mind, the results reported from this point forward make use of the MMÅ2 induced charge polarization model.

Next, we use our one-electron model to extract the NVCB anions of CNs C$_{600}$, C$_{2400}$, and C$_{5400}$ and PAHs C$_{600}$H$_{60}$, C$_{2400}$H$_{120}$, and C$_{5400}$H$_{180}$. Figures 23, 24, and 25 plot the orbitals, EBEs, and
symmetries of the first few bound NVCB states predicted by the one-electron model. The NVCB anions of CNs are obtained in the absence of electrostatics, while the NVCB anions of PAHs include an electrostatic contribution modeled via the $Q_{20}$ quadrupole + edge CH dipole model described in chapter 4. The anions are obtained using the combination of model inducible atomic charges and dipoles. All calculations include the contributions of repulsive atomic Gaussians.
Figure 23: EBEs in meV and single particle orbitals for the NVCB anion states predicted for C\textsubscript{600} and C\textsubscript{600}H\textsubscript{60}. Inducible atomic charges and dipoles\textsuperscript{202} are used for both systems. Model electrostatics are included for C\textsubscript{600}H\textsubscript{60} via an out-of-plane quadrupole on every carbon atom and a dipole on each edge CH group (see chapter 4). Repulsive atomic Gaussians are present for both C\textsubscript{600} and C\textsubscript{600}H\textsubscript{60}. Orbitals are plotted at 90\% charge enclosure of the excess electron’s density using VMD.\textsuperscript{134} The orbital labels are based on the hydrogenic orbitals that they resemble. Symmetry labels and EBEs for anions that are energetically degenerate (or nearly degenerate) are listed within the same row separated by a comma. If the symmetry of a state is unclear it is designated by ?. 
Figure 24: EBEs in meV and single particle orbitals for the NVCB anion states predicted for C\textsubscript{2400} and C\textsubscript{2400}H\textsubscript{120}. See figure 23 for details regarding model potential components employed for CNs and PAHs as well as information about the symmetry labels applied to single particle orbitals.
Figure 25: EBEs in meV and single particle orbitals for the NVCB anion states predicted for C_{5400} and C_{5400}H_{180}. See figure 23 for details regarding model potential components employed for CNs and PAHs as well as information about the symmetry labels applied to single particle orbitals.

One can see in figures 23, 24, and 25 that the 1s NVCB anion persists as the ground state, the 2p_x and 2p_y pair as the first two excited states, and the 3d_{xy} and 3d_{x^2−y^2} pair as higher excited
states for these larger CNs and PAHs. Other excited states with radial or in-plane nodes resembling 
hydrogenic orbitals (e.g., 2s, 3p_y/3p_x, 4f_y(3x^2−y^2)/4f_y(x^2−3y^2), and 5g_{x^4+y^4}) are extracted as well. 
Although, some of the excited states with radial or in-plane nodes appear to have broken or an 
unclear symmetry (e.g., 3d_{xy}-like and 4f_x(x^2−3y^2)-like roots for C_{2400} in figure 24 as well as the three 
highest energy roots for C_{5400} in figure 25). The appearance of these excited states with broken 
symmetries is related to the numerical issues discussed earlier in this manuscript. Unlike the smaller 
PAHs, these larger systems are capable of binding excited state NVCB anions with nodes normal to 
the carbon atom plane (e.g., 2p_z, 3d_{xz}, 3d_{yz}, . . . ). As will be discussed later on, the appearance of a 
2p_z anion is relevant for assessing whether the NVCB anions predicted by our model evolve into 
IPSs for sufficiently large systems.

First, we turn our attention to the NVCB anions of CNs. The energetic ordering of states may 
seem strange at first given that d-like or even f-like roots with in-plane nodes fall below the 2p_z 
root. The 2p_z anionic state lies right above the 2p_x and 2p_y states for C_{600} and C_{2400} in figures 23 
and 24 respectively. Conversely, the 2p_z anionic state is not located within the first twenty NVCB 
states of C_{5400} in figure 25.

A very crude, but surprisingly effective model for understanding this phenomenon is the particle 
in a rectangular box. As one stretches two dimensions of the box (L_x and L_y to be consistent with the 
spatial orientation of the CNs and PAHs) while keeping the third dimension (L_z) fixed, the ground 
state is always 1s (n_x,n_y,n_z = (1,1,1)) and the 2p_x and 2p_y roots (n_x,n_y,n_z = (2,1,1) = (1,2,1)) are 
always the first set of excited states. As the box is stretched further in the x and y dimensions, 
the energy of states is ordered such that quantum number n_z is the slowest moving index, and 
all combinations of n_x and n_y appear before the next value of n_z is reached. The particle in a 
rectangular box is an oversimplification of the potential associated with these CNs, which looks 
roughly cylindrical in the absence of model electrostatics (see figure 26). Despite its simplicity, this 
approximation reveals that three distinct series of anionic states emerge as the size of the CNs grow: 
a series with nodes in the carbon atom plane, a series with nodes normal to the carbon atom plane, 
and a series with nodes in both dimensions. Furthermore, the inherent two-dimensional nature of 
these planar carbon systems stabilizes the anions with in-plane nodes more than those with nodes 
normal to the carbon atom plane.

Once electrostatics are included in the model potential for the PAHs, the trends observed for
CNs change qualitatively. The 1s-like anion, 2p_x and 2p_y states, and planar d-like states (3d_{xy}, 3d_{x^2−y^2}) observed for the CNs are all present for the PAHs and retain a similar energetic ordering. However, the EBEs of the PAHs are smaller than that of the CNs, indicating that electrostatics destabilize the binding of all anions considered. Additionally, the electrostatics alter the single particle orbitals appreciably.

In figure 23 it can be seen that there is a higher probability of finding the excess electron near the periphery of C_{60}H_{60} when compared to the anionic states of C_{60}. The orbitals of the NVCB states of C_{60}H_{60} place more weight near the edge CH bonds than do those of C_{60}. The d-like anionic state with nodes normal to the plane of carbon atoms that was present for C_{60} vanishes for C_{60}H_{60}. Comparing the anions of C_{60}H_{60} to those of C_{2400}H_{120}, one sees the effects of electrostatics reverse. The single particle orbitals of C_{2400}H_{120} in figure 24 no longer exhibit an enhanced attraction of the excess electron to the edge CH bonds, rather they become more confined to the carbon atom plane. This effect is particularly dramatic for the 1s, 2p_x, 2p_y, and 2p_z states. This electrostatic confinement effect becomes even more prominent for the ground and excited state orbitals of C_{5400}H_{180}.

A separate, but related effect of electrostatics is the stabilization of the excited state 2p_z anion relative to those with in-plane nodes. In figure 23 one can see that the 2p_z state is the highest energy excited state of C_{2400}, but it drops just above the 2s state for C_{2400}H_{120}. Similarly, in figure 24 the 2p_z root does not appear within first the nineteen excited states of C_{5400}, but it drops to the fourteenth excited state for C_{5400}H_{180}. This trend is the converse of what was observed for CNs and requires more information than the crude particle in a rectangular box model can provide.

To better understand this spatial confinement of NVCB states on large PAHs, we plot slices of our model potential with (PAHs) and without (CNs) electrostatics in figure 26. One-dimensional slices of the potentials are taken along the y axis at heights of z = 3, 6, and 9 above the carbon atom plane of CNs C_{60} and C_{2400} and PAHs C_{60}H_{60} and C_{2400}H_{120}.
Figure 26: One-dimensional slices of the model potential for a negative point charge (e\(^{-}\)) interacting with CNs: C\(_{600}\) and C\(_{2400}\) as well as PAHs: C\(_{600}H_{60}\) and C\(_{2400}H_{120}\). Solids lines represent the potential associated with CNs and dashed lines the potential associated with PAHs. All images represent a slice along y axis. The distance of the slice above the plane of atoms (z) is fixed at 3 (black lines), 6 (red lines), and 9 (yellow lines) a.u. All lines include the model potential contributions from inducible atomic charges and dipoles and repulsive atomic Gaussians. In addition to the above model components, the potential of PAHs include electrostatics via an out-of-plane quadrupole on every carbon atom and dipole on every edge CH pair (see chapter 4).

The slices of the model potentials in figure 26 exhibit a few features that add context to the relative impact of polarization and electrostatics. Comparing the model potentials of C\(_{600}\) (solid lines) and C\(_{600}H_{60}\) (dashed lines) one can see that electrostatics are a repulsive contribution above and below the carbon atom plane for this smaller PAH. The model potential slices at z = 6 (red lines) and z = 9 (yellow lines) a.u. show that electrostatics repulse the electron above the carbon atom plane (\(-44 < y < 44\)) and attract it at the hydrogen terminated edges (\(y \geq 44\) and \(y \leq -44\)). Closer to the surface of the CN and PAH at z = 3 a.u., the electrostatic repulsion above the carbon plane is overwhelmed by the polarization potential and another local minima forms at the center of the PAH, producing the black dashed line. These features in the model potential of C\(_{600}H_{60}\) are very similar to what was observed in our previous study on smaller PAHs (see chapter 3\(^{181}\)), so it is no surprise
that the electrostatic driven edge localization appears for C$_{600}$H$_{600}$ as well.

The polarization potentials of C$_{2400}$ (solid lines) and C$_{2400}$H$_{120}$ (dashed lines) are considerably stronger than C$_{600}$ and C$_{600}$H$_{60}$ leading to a distinctly different set of curves. One can still see some repulsion of the excess electron above the carbon atom plane ($y \geq 86$ and $y \leq -86$) and attraction at the edges of ($-86 < y < 86$) C$_{2400}$H$_{120}$ in slices taken at $z = 6$ and $z = 9$ a.u. However, the effect is much less pronounced yielding curves that are relatively flat above the carbon atom plane. Closer to the surface of the PAH at $z = 3$ a.u., the electrostatics are dwarfed by the polarization near the center of the carbon atom plane. Moving outward towards the edges of the PAH the effects of electrostatics reappear causing the potential to increase and decrease briefly at the hydrogen terminated edges.

Figure 26 illustrates how our model potential can drive an excess electron to the hydrogen terminated edges of small PAHs and confine them above and below the carbon atom plane of large PAHs. The relative contributions of polarization and electrostatics produce a potential, which is more attractive at the center than edges of large PAHs. This also explains why the 2$p_z$ root appears earlier in the excited state series of large PAHs than CNs of the same size. Confining this state to the space around the center of the carbon plane is energetically cheaper than those with many in-plane nodes.

Now, we evaluate the connection between the IPSs of graphene and the NVCB anions of the finite PAHs we have characterized. Past theoretical studies employing the, “LDA+Image Potential,” approach in periodic boundary condition (PBC) calculations predicted that the first two IPSs have one node above and one below the graphene plane.$^{27,28}$ They identified the even ground state IPS as being symmetric with respect to reflection through the carbon atom plane ($1^+$) and the odd ground state IPS as being antisymmetric ($1^-$). These characteristics are similar to the 1$s$ ground and 2$p_z$ excited NVCB states we have characterized for the finite systems above. The only trait absent from our model NVCB states is the additional node above and below the plane of atoms. However, this much is expected as our model implicitly includes the energetic impact of orthogonalization of NVCB states to the occupied states of the neutral molecules via a repulsive pseudopotential. Without explicitly including the electrons of the PAHs in our model, which completely defeats its purpose, we will never observe these orthogonalization effects in the wavefunctions produced by our one-electron model. We expect that in an all-electron calculation of the 1$s$ ground and 2$p_z$ excited NVCB states, the nodal surface would resemble that of the $1^+$ and $1^-$ IPSs.
Having identified NVCB states that resemble the first two IPSs, we use the EBEs collected for the 1s and 2p\textsubscript{z} NVCB states to perform an extrapolation. The extrapolation procedure includes the ebes of all CNs and PAHs considered (C\textsubscript{6n\textsuperscript{2}} and C\textsubscript{6n\textsuperscript{2}}H\textsubscript{6n} where n = 10, 12, 15, 20, 25, 30), not just those in shown in figures 23, 24, and 25.

Figure 27: Extrapolation of one-electron model binding energies (EBEs) in meV for the 1s and 2p\textsubscript{z} NVCB anions of CNs and PAHs with respect to 1/n, where n refers to the index in the following chemical formulae C\textsubscript{6n\textsuperscript{2}} and C\textsubscript{6n\textsuperscript{2}}H\textsubscript{6n}. Filled circles and squares represent the EBEs of PAHs and CNs respectively. Binding energies are extrapolated backwards to the y-axis (lim\textsubscript{n→∞} 1/n), which represents the model estimates of graphene’s first even and odd IPS. Polynomial functions of the form ax\textsuperscript{2} + bx + c are fit to the EBE data using the curve_fit module of the Python library SciPy.\textsuperscript{135} See the text for details on the model potential components used.

The y-intercepts of the polynomial fits in figure 27, represent our one-electron model’s EBE estimates for the 1\textsuperscript{+} and 1\textsuperscript{−} IPSs. The extrapolation procedure predicts that the EBEs of PAHs (filled circles) converge to energetically larger estimates of the 1\textsuperscript{+} and 1\textsuperscript{−} IPSs relative to their CN counterparts (filled squares). These results imply that the confinement introduced by electrostatics enhances the binding energies of the 1\textsuperscript{+} and 1\textsuperscript{−} IPSs. This is surprising, as one would expect that the effects of electrostatics become negligible for infinitely large sheets of carbon atoms. However, the largest system treated in this work consists of 5400 carbon atoms spanning a radius of \textasciitilde 7 nm. This is quite small when compared to the pristine, single layer graphene sheets used in experimental settings, which can span multiple nanometers to a few micrometers. At this juncture, we are
more willing to ascribe this unexpected result to the limited set of data points in our extrapolation procedure. It is entirely possible that extracting EBEs for larger PAHs and CNs, will remove this unexpected behavior producing extrapolated estimates which agree regardless of electrostatics.

Finally, we compare the extrapolated EBEs of our model to the results of PBC calculations,\textsuperscript{27,28} as well as 2PPE measurements.\textsuperscript{192,193} We tabulate all these binding energies in table 5 below.

Table 5: Electron binding energy electron binding energy (EBE) in eV for the first even and odd image potential state (IPS) of graphene as predicted by our one-electron model, periodic boundary condition (PBC) LDA+Image Potential calculations from publication [27] and [28], and two-photon photoemission spectroscopy experiments from publications [192] and [193]. See the text for details on the potential components used in our one-electron model calculations. The LDA+Image Potential calculations of publications [27] and [28] employed a hybrid exchange-correlation potential stitching together the short-range LDA functional with the image potential $-1/4|z - z_{im}|$ at matching point $z_0$ above the carbon atom plane. The authors of publication [27] defined the image plane to be $z_{im} = 0$, while the authors of publication [28] tested values of $z_{im} = 1.048$ Å and $(z_{im} = -1.048)$ Å.

<table>
<thead>
<tr>
<th>IPS</th>
<th>One-electron model</th>
<th>PBC LDA+Image Potential $z_0$[27]</th>
<th>PBC LDA+Image Potential $z_0$[28]</th>
<th>2PPE Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.6</td>
<td>2.1</td>
<td>2.6</td>
</tr>
<tr>
<td>$1^+$</td>
<td>0.863</td>
<td>1.47</td>
<td>1.33</td>
<td>1.29</td>
</tr>
<tr>
<td>$1^-$</td>
<td>0.736</td>
<td>0.72</td>
<td>0.61</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Before making comparisons, the variety of EBE data presented in table 5 warrants some explanation. The first two sets of PBC calculations\textsuperscript{27,28} (second and third columns) make use of a hybrid LDA+Image Potential with the following form,

$$V(r) = \begin{cases} 
V_{xc}^{LDA}(r), & \text{for } z_0 > |z| \\
-\frac{1-A(x,y)e^{-\lambda(x,y)|\text{sgn}(z)z_{im}|}}{4|z - \text{sgn}(z)z_{im}|}, & \text{for } |z| > z_0 
\end{cases}$$  \hspace{1cm} (69)$$

where $z$ is the height above or below the carbon plane, $z_{im}$ is the image plane position, and $z_0$ is a cutoff at which the short-range LDA exchange-correlation potential ($V_{xc}^{LDA}(r)$) switches to the
modified form of the image potential. The terms $A(x,y)$ and $\lambda(x,y)$ are parameters included to ensure a smooth transition between the short-range LDA potential and image potential at point $z_0$. The correct value of $z_0$ is not known, so the authors of publications $a^{27}$ and $b^{28}$ both calculated the IPS binding energies at values of $z_0 = 1.6, 2.1, 2.6 \ \text{Å}$, with different values of $z_{im}$ (see the table caption for details). The last two columns from publications $c^{192}$ and $d^{193}$ show the binding energies of the first two IPSs obtained by fitting the 2PPE spectrum of pseudo-free standing graphene on a SiC substrate.

The binding energies predicted by our one-electron model for graphene’s $1^+$ and $1^-$ IPSs agree fairly well. Our model’s binding energy for the $1^+$ is weaker than the 2PPE and LDA+Image Potential results. However, it is worth mentioning that the $1^+$ state is strongly bound relative to $1^-$ and more highly excited IPSs making it particularly sensitive to the nature of the short-range potential.$^{185}$ Moreover, both 2PPE experiments measured binding energies of the $1^+$ state that lie below the LDA+Image Potential calculations. Conversely, the binding energy predicted by our model for the $1^-$ IPS falls in line with both the LDA+Image Potential and 2PPE results. Thus, we do not take the comparatively weak binding of the $1^+$ state in our one-electron model as evidence of failure to capture the essential physics. Rather, it suggests the need to refine the short-range repulsive potential and extract the ground state EBE of larger systems.

6.6 Conclusions

In this article, we presented results demonstrating that the image potential states of graphene and the non-valence correlation bound (NVCB) anions of its finite analogs are fundamentally the same. We simulated the NVCB anions of PAHs ranging in size from tens to thousands of atoms using a model one-electron Hamiltonian, where the charge distributions of polycyclic aromatic hydrocarbons ($C_{6n^2}H_{6n}$) are represented via classical electrostatic, polarization, and repulsion potentials parameterized on quantum mechanical data. RPA calculations support the ground and excited state NVCB anions our one-electron model produces for the PAHs $C_{54}H_{18}$ and $C_{96}H_{24}$. We observe a variety of unique excited state NVCB anions for PAHs $C_{6n^2}H_{6n}$ $n = 3$ to $7$ with wavefunctions resembling the hydrogenic $2s, 2p, 3d$, and $4f$ orbitals. Excited NVCB anions with
nodes normal to the carbon atom plane were observed for PAHs of size \( n = 10, 12, 15, 20, 25, \) and 30. Our one-electron model produces a \( 1s \) ground state and \( 2p_z \) excited state anion reminiscent of graphene’s \( 1^+ \) and \( 1^- \) image potential states. Extrapolation of the EBE data collected for the \( 1s \) ground and \( 2p_z \) excited NVCB states to the limit of an infinite graphene sheet yields binding energies for the \( 1^+ \) and \( 1^- \) IPSs that agree reasonably well with past PBC calculations and two-photon photoemission spectroscopy experiments. When model electrostatics are neglected and the edge hydrogen atoms are stripped from the PAHs, we observe a qualitative change in the binding energies and single particle orbitals of the ground and excited state NVCB anions. Future work includes a refinement of the repulsive potential, refactoring of the diagonalization routines, implementing symmetry adapted DVR basis functions, and an extension of these calculations to even larger systems.

### 6.7 Acknowledgements

We acknowledge support from the US National Science Foundation under grant number CBET-2028826. This research was supported in part by the University of Pittsburgh Center for Research Computing, RRID:SCR_022735, through the resources provided. Specifically, this work used the H2P cluster, which is supported by NSF award number OAC-2117681.
7.0 Conclusions

This work documents progress towards developing a one-electron model for the NVCB anions of hexagonal PAHs belonging to the chemical series $C_{6n^2}H_{6n} \ n = 1, 2, 3, \ldots$, spanning tens to thousands of atoms in size. The one-electron model describes the interaction of an excess electron with the PAHs via classical polarization, repulsion, and electrostatic potentials parameterized on quantum mechanical data. The parameterization process involves all-electron calculations that provide insight into the nature of static and perturbation dependent properties of PAHs and how they scale with system size. This approach enables the prediction and characterization of NVCB anions of molecules that would be inaccessible to the quantum mechanical methods which are routinely applied to these non-valence anions.

In chapter 3 we characterized the lowest energy NVCB anion and properties of the polycyclic aromatic hydrocarbon (PAH)s $C_{6n^2}H_{6n} \ n = 3$ to 7. Good agreement was observed between the dipole polarizabilities and polarization potentials of our model and those from PBE0 and MP2 calculations. It was found that inducible charges are central to obtaining accurate dipole polarizabilities and polarization potentials within our model. Qualitative trends in the EBE reveal that electrostatics are destabilizing to the ground state NVCB anion and plots of the excess electron’s charge density exhibit a shift toward the periphery of the ring systems.

In chapter 4 we studied the electrostatic properties of polycyclic aromatic hydrocarbon (PAH)s ranging in size from six to fifteen thousand carbon atoms with the goal of constructing a minimal atomic multipole model for large graphene nanoflakes. Atomic multipole moments were calculated using GDMA and BS-ISA, which yield appreciably different results. Based on the accuracy and rapid convergence of the BS-ISA multipole expansion, we believe that it provides a more useful description of electrostatics than the GDMA procedure. BS-ISA predicts a near zero quadrupole moment ($Q_{20}^C \sim -0.006$) for a carbon atom in graphene, from which we conclude that the $Q_{20}^C$ value for graphite measured by Whitehouse and Buckingham\textsuperscript{162} derives predominantly from edge dipoles. This conclusion was supported via model calculations which demonstrate that the edge CH dipoles constitute a sizable contribution to the electrostatic potential above the central ring of graphene nanoflakes as large as $C_{15000}$. 

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In chapter 5 we refined the model polarization potential developed in chapter 3 to study the polarization properties of carbon nanoflakes consisting of tens-of-thousands of atoms. We applied our atomic inducible charge polarization model to the $C_{60000}$ carbon nanoflake and found excellent agreement with the classical image potential and induced charge distribution of a conducting sheet. The inclusion of atomic inducible dipole terms in our model produced an estimate of $z_{\text{im}} = 1.3334 \, a_0$ for graphene’s image plane, which agrees with existing estimates in the literature. We calculated the interaction of two charges on opposite sides of $C_{60000}$ and by testing opposing and like signs of the external charges, we concluded that an atomically thin molecule does not screen their Coulomb interaction. These results demonstrated that it is possible to model the polarization behavior of graphene via large finite analogues.

In chapter 6 we used our refined polarization and electrostatic models in our one-electron Hamiltonian to study the ground and excited state NVCB anions of PAHs ranging in size from tens to thousands of atoms. We observed excited state NVCB anions for PAHs $C_{6n^2}H_{6n}$ $n = 3$ to $7$ with wavefunctions resembling the hydrogenic $2s$, $2p$, $3p$, $3d$, $4f$, and $5g$ orbitals. Our one-electron model predicts $1s$ and $2p_z$ NVCB anion states for PAHs $C_{600}H_{60}$, $C_{864}H_{72}$, $C_{1350}H_{90}$, $C_{2400}H_{120}$, $C_{3750}H_{150}$, and $C_{5400}H_{180}$, which have wavefunctions reminiscent of graphene’s $1^+$ and $1^-$ IPSs. Extrapolation of the EBE data collected for the $1s$ ground and $2p_z$ excited NVCB states to the limit of an infinite graphene sheet yielded binding energies in reasonable agreement with past PBC calculations$^{27,28}$ and 2PPE experiments$^{192,193}$ on the $1^+$ and $1^-$ IPSs. Future work includes further refinements of the model potentials, a refactoring of the numerical routines used for diagonalizing the Hamiltonian, and the implementation of symmetry adapted DVR basis functions. With these improvements in place we hope to extend these calculations to even larger systems and selectively extract NVCB anions that resemble higher excited state roots in the image potential series. The incorporation of electrostatic edge effects via terminal hydrogen bonds can be viewed as a first order correction to the idealized model of a defect free infinite graphene sheet routinely applied in PBC calculations of IPSs. Two obvious extensions of this work are the exploration of edge termination by atoms other than hydrogen and the study of three-dimensional PAH clusters which represent finite analogs of bilayer and trilayer graphene. A non-trivial, but worthwhile extension is the incorporation of structural defects (e.g. Stone-Wales, single vacancy, multiple vacancy, etc.) commonly encountered in experimental samples.$^{214}$ Inclusion of these
structural modifications would constitute considerable changes to the model potentials developed in this thesis, but provide opportunities to study how these loosely bound anions might localize near such defects.

On a closing note, I hope that this work will generate more interest in NVCB anions and IPSs amongst the quantum chemistry and condensed matter physics communities. The large, but finite molecules probed in this thesis occupy a gray area at the intersection of these two scientific communities. As a consequence, there is a scarcity of benchmark theoretical results and experimental measurements. Interdisciplinary collaborations will be crucial, if not necessary, to further our understanding of these fascinating anions.
Appendix A Additional Works

During the course of my graduate studies I was fortunate to receive exciting research opportunities outside the projects contributing to my thesis. This appendix contains a publication that arose from an interdisciplinary collaboration with the Tang group and Yang group from the University of Pittsburgh’s School of Computing and Information and School of Electrical and Computer Engineering respectively. It is well known that physical quantum computers are currently expensive to engineer and run, in high demand, and limited in their capabilities. An alternative to using physical quantum computers, is simulating them on the classical hardware in environments that obey the theoretical principles of quantum hardware. This approach enables the scientific community to develop new algorithms for and study chemical systems on simulated quantum hardware. However, depending on the quantum computing algorithms applied one can rapidly approach the limit of what a classical computer can handle making efficient simulation of quantum computing environments relevant. With the computer science expertise provided by the Yang group and Tang group, this collaborative effort implemented a framework (named Q-GPU) into the QISKit package which utilizes both CPU and GPU resources to enable the efficient simulation of tens of qubits.

A.1 Q-GPU: A Recipe of Optimizations for Quantum Circuit Simulation Using GPUs

The text and figures in this chapter have been adapted from: Y. Zhao et al., “Q-GPU: A Recipe of Optimizations for Quantum Circuit Simulation Using GPUs,” *International Symposium on High-Performance Computer Architecture*, 2022, pp. 726-740, DOI: 10.1109/HPCA53966.2022.00059 with the permission of IEEE. The author’s contribution to the work included running timings for the hydrogen chain sample circuit as well as writing and editing portions of the manuscript.
A.1.1 Summary

In recent years, quantum computing has undergone significant developments and has established its supremacy in many application domains. Unfortunately, modern quantum computing is still positioned in the Noisy Intermediate-Scale Quantum (NISQ) era that is limited by the number of qubits, short qubit lifetime, and imperfect operations. While quantum hardware is accessible to the public through the cloud environment, a robust and efficient quantum circuit simulator is necessary to investigate the constraints and foster quantum computer development, such as quantum algorithm development and quantum device architecture exploration. In this paper, we observe that most of the publicly available quantum circuit simulators (e.g., QISKit from IBM) are not optimized and suffer from slow simulation and poor scalability. To this end, we systematically studied the deficiencies in modern quantum simulators and propose Q-GPU, a framework that leverages GPUs with comprehensive optimizations to allow efficient and scalable quantum circuit simulation (QCS). Specifically, Q-GPU features i) proactive state amplitude transfer, ii) zero state amplitudes pruning, iii) delayed qubit involvement, and iv) non-zero state compression. Experimental results across eight representative quantum circuits indicate that Q-GPU significantly improves the simulation performance over the state-of-the-art GPU-based QCS by $2.53 \times$ on average. It also outperforms the most recent OpenMP CPU implementation, the Google Qsim-Cirq simulator, and the Microsoft QDK simulator.

A.1.2 Introduction

Quantum computing is a promising computing paradigm that has the potential to solve problems that cannot be handled by classical computers in a feasible amount of time.\(^{216}\) In the past decade, there has been steady progress towards building a large quantum computer. The number of qubits in a real quantum machine has increased from 14 in 2011\(^ {217}\) to 76 in 2020.\(^ {218}\) IBM promises 1000 qubits quantum machine by the year 2023.\(^ {219}\) Despite this rapid progress, current quantum computing is still positioned in the Noisy Intermediate-Scale Quantum (NISQ) era where the public has very limited access to quantum machines. These machines are also constrained by the limited number of qubits, short lifetimes of qubits, and imperfect operations.\(^ {220}\) Thus, quantum circuit simulation (QCS) toolsets provide an essential platform to satisfy many needs, e.g., developing
many different algorithms with a large number of qubits, validating and evaluating newly proposed quantum circuits, and design space exploration of future quantum machine architectures. Many companies, such as IBM, Google, Intel, and Microsoft have developed their quantum circuit simulators to provide precise end-end simulation.

In general, QCS is challenging as it is both compute-intensive and memory-intensive. The reasons are: i) fully and accurately tracking the evolution of quantum system through classical simulation requires storing all the quantum state amplitudes, which carries a memory cost that grows exponentially as the number of qubits in the simulated quantum circuit increases, and ii) applying a gate within a quantum circuit requires a traversal of all the stored state amplitudes, leading to exponentially scaling computational complexity. Modern GPUs have been used to fuel QCS in high-performance computing (HPC) platforms. Specifically, when applying a gate to a \( n \)-qubit quantum circuit, the \( 2^n \) state amplitudes are evenly divided into groups, and each group of amplitudes is updated independently in parallel by GPU threads. However, the promising parallelism of GPUs is diminished by the limited GPU on-board memory capacity. For example, simulating a quantum circuit with 34 qubits requires 256 GB of memory to store state amplitudes, which is beyond the memory capacity of any modern GPUs.

There exist several works optimizing QCS, including multi-GPU supported simulation, OpenMP and MPI based CPU simulation, and CPU-GPU collaborative simulation. Most of these works focus on distributed simulation while failing to benefit from GPU execution due to the memory constraint. In particular, our characterization shows that the state-of-the-art GPU-based simulation has low GPU utilization when the number of qubits in the quantum circuit is large. As a result, most state amplitudes are stored and updated on the CPU, failing to take advantage of the GPU parallelization. Moreover, the static and unbalanced allocation of state amplitudes introduces frequent amplitude exchange between CPU and GPU, which introduces additional data movement and synchronization overheads.

In this paper, we aim to provide a high-performance and scalable QCS using GPUs. We propose \( Q\text{-GPU} \), a framework that significantly enhances the simulation performance for practical quantum circuits. The proposed framework leverages modern GPUs as the main execution engine and is featured with several end-to-end optimizations to fully take advantage of the rich computational parallelism on GPUs, while maintaining a minimum amount of data movement between the CPU and
GPU. Specifically, our approach includes four optimizations. First, instead of statically assigning state amplitudes on GPU and CPU as done in prior works,\textsuperscript{229} Q-GPU dynamically allocates groups of state amplitudes on the GPU and proactively exchanges the state amplitudes between CPU and GPU. Doing so maximizes the overlap of data transfer between CPU and GPU, thereby reducing the GPU idleness. Second, Q-GPU prunes zero state amplitudes to avoid unnecessary data movement between CPU and GPU. Third, we also propose compiler-assisted quantum gate reordering (complying with the gate dependencies) to enlarge the opportunity of pruning zero state amplitudes. Finally, we propose efficient GPU-supported lossless data compression to further reduce data transfer caused by non-zero amplitudes. This paper makes the following contributions:

- We use the popular IBM QISKit-Aer with its state-of-the-art CPU-GPU implementation,\textsuperscript{215} and conduct an in-depth characterization of the simulation performance. We observe that the performance degrades significantly as the number of qubits increases due to the unbalanced amplitudes assignment, where most of the computation is done by the CPU.
- We implement a dynamic state amplitude assignment to allow the GPU to update all state amplitudes. However, such an implementation did not provide any performance improvements and even worsened compared to the CPU execution due to the massive and expensive data movement between CPU and GPU.
- We propose Q-GPU, a framework comprising end-to-end optimizations to mitigate the data movement overheads and unleash the CPU capability in QCS. Specifically, the proposed Q-GPU is featured with the following major optimizations: i) dynamic state amplitudes allocation and proactive data exchange between CPU and GPU, ii) dynamic zero state amplitude “pruning”, iii) dependency-aware quantum gate reordering to enlarge the potential of zero amplitude pruning, and iv) GPU-supported efficient lossless compression for non-zero amplitudes.
- We evaluate the proposed Q-GPU framework using eight practical quantum circuits. Experimental results indicate that in all circuits tested, Q-GPU significantly improves the QCS performance and outperforms the baseline by $2.53 \times$ on average. We also compare Q-GPU with Google Qsim-Cirq\textsuperscript{230} and Microsoft QDK,\textsuperscript{231} and results show that Q-GPU approach outperforms Qsim-Cirq and QDK by $1.02 \times$ and $9.82 \times$, respectively.
A.1.3 Background

A.1.3.1 Quantum Basics

Similar to the bit concept in classical computation, quantum computation is built upon the quantum bit or qubit for short. A qubit is a two-level quantum system defined by two computational orthonormal basis states $|0\rangle$ and $|1\rangle$. A quantum state $|\psi\rangle$ can be expressed by any linear combination of the basis states.

$$|\psi\rangle = a_0 |0\rangle + a_1 |1\rangle,$$

where $a_0$ and $a_1$ are complex numbers whose squares represent the probability amplitudes of basis states $|0\rangle$ and $|1\rangle$, respectively. Note that we have $|a_0|^2 + |a_1|^2 = 1$, meaning that after measurement, the read out of state $|\psi\rangle$ is either $|0\rangle$ or $|1\rangle$, with probabilities $|a_0|^2$ and $|a_1|^2$, respectively. The states of a quantum system are generally represented by state vectors as

$$|0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, |1\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.\quad (71)$$

To be more general, for an $n$-qubit system, there are $2^n$ state amplitudes. Then, the quantum state $|\psi\rangle$ can be expressed as a linear combination

$$|\psi\rangle = a_{00} |00\rangle + a_{01} |01\rangle + \cdots + a_{11} |11\rangle. \quad (72)$$

Similarly, the state of a $n$-qubit system can also be represented by a state vector with $2^n$ dimensions as

$$|\psi\rangle = \begin{bmatrix} a_{00} \\ a_{01} \\ \vdots \\ a_{11} \end{bmatrix}.$$

Quantum computation describes changes occurring in this state vector. A quantum computer is built upon a quantum circuit containing quantum gates (or quantum operations), and a quantum algorithm is described by a specific quantum circuit. In simple terms, quantum gates are represented by unitary operations that are applied on qubits to map one quantum state to another. A quantum gate that acts on $k$ qubits is represented by a $2^k \times 2^k$ unitary matrix.
To illustrate how a quantum gate is applied to a state vector, let us consider a 2-qubit system with a Hadamard gate/operation operating on qubit 0. A Hadamard gate can be represented as

$$H = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}. \quad (74)$$

Then the state vector of this 2-qubit system is updated through

$$\begin{bmatrix} a'_{00} \\ a'_{01} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} a_{00} \\ a_{01} \end{bmatrix}, \quad (75)$$

$$\begin{bmatrix} a'_{10} \\ a'_{11} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} a_{10} \\ a_{11} \end{bmatrix}. \quad (76)$$

For an $n$-qubit system, when a $H$ gate is applied to qubit $j$ the amplitudes are transformed as:

$$\begin{bmatrix} a'_{x\ldots0_j\ldots x} \\ a'_{x\ldots1_j\ldots x} \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} a_{x\ldots0_j\ldots x} \\ a_{x\ldots1_j\ldots x} \end{bmatrix}. \quad (77)$$

Therefore, the indices of every pair of amplitudes have either 0 or 1 in the $j$th bit, while all other bits remain the same\(^1\). Note that each pair of amplitudes can be updated in parallel.

### A.1.3.2 Quantum Circuit Simulation (QCS)

The purpose of QCS is to mimic the dynamics of a quantum system,\(^{223}\) and to reproduce the outcomes of a quantum circuit with high accuracy. There are several approaches to simulating a quantum circuit, each offering different advantages and drawbacks. We summarize the three most widely used approaches below.

- **Schrödinger style simulation:** Schrödinger simulation describes the evolution of a quantum system by tracking its quantum state. It tracks the transformations of the state vector according to Equation 77. Note that one can also track the density matrix $\rho = |\psi\rangle\langle\psi|$, which is useful when measurement is required during simulation.\(^{223,224}\) In this work, we only consider quantum measurements at the end of circuits.

\(^1\)“×” can be 0 or 1; the “×” in the same position of $a_{x\ldots\times0\ldots x}$ and $a_{x\ldots\times1\ldots x}$ are the same.
• **Stabilizer formalism:** Simulation based on the stabilizer formalism is efficient for a restricted class of quantum circuits. Specifically, stabilizer circuits (a.k.a Clifford circuits) can be simulated in $O(poly(n))$ space and time costs. Rather than tracking the state vector, the quantum state is uniquely represented and tracked by its stabilizers, which is essentially a group of operators derived from the Clifford group. A detailed description can be found in.

• **Tensor network:** Tensor network simulators are useful when a single or few amplitudes of the full state vector are being updated as tensor networks. For example, one type of tensor network that are extremely common are matrix product states (MPS). When applied to a single amplitude in Equation 72, the resulting state resembles a long string of matrix multiplications

$$\left| \psi \right\rangle = \sum_{j_0 \cdots j_{n-1} j_n} a_{j_0 \cdots j_{n-1} j_n} \left| j_0 \cdots j_{n-1} j_n \right\rangle$$

$$= \sum_{j_0 \cdots j_{n-1} j_n} Tr[A_{j_0} \cdots A_{j_{n-1}} A_{j_n}] \left| j_0 \cdots j_{n-1} j_n \right\rangle$$

The matrices $A$ (rank-2 tensors) in Equation 79 can be thought of as a decomposition of the full coefficient tensor $a$. Despite the restriction of returning a limited number of amplitudes, tensor networks states are efficient as they compress the dimension of the problem from $O(2^n)$ to $O(nd^2)$ where $d$ is the dimension of the individual tensors in Equation 79.

Among all these simulation methods, Schrödinger style simulation is widely used as the mainstream simulation method, and has been widely adopted in prior research works. Also, industrial quantum circuit simulators such as IBM Qiskit, Google Qsim-Cirq and Microsoft QDK use full state vector simulations. In this work, we build Q-GPU based on IBM Qiskit-Aer, a high-performance C++ simulation backend of Qiskit, since it contains the state-of-the-art GPU support.

### A.1.4 Characterization of QCS

#### A.1.4.1 Quantum Circuit Benchmarks

In this paper, we characterize the performance of QCS using a rich set of quantum circuits. Table 6 lists the circuit benchmarks.

- **hchain:** This circuit which describes a system of hydrogen atoms arranged linearly is a representative quantum chemistry application. This circuit incorporates increased circuit
Table 6: List of quantum circuit benchmarks

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>hchain</td>
<td>Linear hydrogen atom chain\textsuperscript{243}</td>
</tr>
<tr>
<td>rqc</td>
<td>Random quantum circuit\textsuperscript{216}</td>
</tr>
<tr>
<td>qaoa</td>
<td>Quantum approximate optimization algorithm\textsuperscript{244}</td>
</tr>
<tr>
<td>gs</td>
<td>Graph state\textsuperscript{245,246}</td>
</tr>
<tr>
<td>hlf</td>
<td>Hidden linear function\textsuperscript{247}</td>
</tr>
<tr>
<td>qft</td>
<td>Quantum Fourier transform\textsuperscript{248}</td>
</tr>
<tr>
<td>iqp</td>
<td>Instantaneous quantum polynomial-time\textsuperscript{249,250}</td>
</tr>
<tr>
<td>qf</td>
<td>Quadratic form\textsuperscript{251}</td>
</tr>
</tbody>
</table>

depth and an early entanglement in terms of total operations.

- **rqc**: The random quantum circuit from Google\textsuperscript{216,257} is used to represent the quantum supremacy compared to classical computers.

- **qaoa**: Quantum approximate optimization is a promising quantum algorithm in the NISQ era that produces approximate solutions for combinatorial optimization problems.\textsuperscript{244}

- **gs**: This circuit is used to prepare graph states\textsuperscript{258} that are multi-particle entangled states. Examples include many-body spin states of distributed quantum systems that are important in quantum error correction.\textsuperscript{259}

- **hlf**: This benchmark circuit solves the 2D hidden linear function problem.\textsuperscript{247}

- **qft**: The quantum Fourier transform circuit\textsuperscript{248} is the quantum analog of the inverse discrete Fourier transform. It is an important function in Shor’s algorithm.\textsuperscript{260}

- **iqp**: The instantaneous quantum polynomial circuit provides evidence that sampling the output probability distribution of a quantum circuit is difficult when using classical approaches.\textsuperscript{249,250}
• \textbf{qf}: This circuit implements a quadratic form on binary variables encoded in qubit registers. It is used to solve the quadratic unconstrained binary optimization problems.\textsuperscript{251}

\section*{A.1.4.2 Baseline QCS}

\textbf{Step 1: State vector partitioning:} QISKit-Aer first partitions the state vectors into "chunks". Chunk is the granularity used in the simulator to update the state vector. For illustrative purposes, let us assume we have a 7-qubit circuit, i.e., that there are in total $2^7$ different state amplitudes from $a_{0000000}$ to $a_{1111111}$. All the states are stored in a vector (i.e., the state vector), and this state vector is partitioned into chunks. For example, assuming we divide the state vector into 8 chunks, each chunk contains 16 state amplitudes as shown in Figure 28. The three most significant bits are used to index the chunks, and the remaining bits are as offsets within a chunk.

\textbf{Step 2: Static chunk allocation:} After partitioning, these chunks are allocated into GPU memory based on the GPU memory availability. As illustrated in Figure 28, if a GPU can only store 3 chunks, the remaining 5 chunks will be stored in the host CPU memory. For example, when 64 GB memory is needed to simulate 32 qubits, the first 16 GB is allocated in GPU memory (in P100 GPU with 16 GB memory) and the remaining 48 GB is in the CPU memory.

\textbf{Step 3: Reactive chunk exchange:} During circuit simulation, a chunk exchange between the GPU and the CPU arises when the requested state amplitudes are not locally available on the GPU. In QISKit-Aer, the chunk exchange between the CPU and the GPU is triggered on-demand. That is, when both the chunks on the CPU and the GPU are involved in one state-update calculation, the corresponding CPU chunks are transferred to GPU for updating. After the operation, the updated chunks are transferred back to the CPU. Note that, the amount of data exchange in the following scenarios is dependent on the qubits in the specific gate simulation.

- \textbf{Case 1: All the indices of the qubits involved in the current gate are smaller than the chunk size:} For example, a gate on qubit 0 requires amplitudes $a_{\times\times\times\times\times\times0}$ and $a_{\times\times\times\times\times\times1}$ (see Equation 77). In this case, each chunk can be updated independently without requiring extra data movement.
- \textbf{Case 2: Some indices of qubits involved in the current gate are outside the chunk boundary:} In this scenario, let us assume there is a gate that operates on $q_6$, thereby the required pairs
of amplitudes are $a_{x0\times\cdots\times}$ and $a_{x1\times\cdots\times}$. However, as depicted in Figure 28, none of the chunks contains a pair of required amplitudes, i.e., the computation for updating amplitudes involves more than one chunk. Specifically, to update the pairs of amplitudes, we need $(\text{chunk}_0, \text{chunk}_2)$, $(\text{chunk}_1, \text{chunk}_3)$, …, and $(\text{chunk}_5, \text{chunk}_7)$. However, $(\text{chunk}_1, \text{chunk}_3)$ involves one chunk on the GPU and one chunk on the CPU. In this scenario, data exchange is required. In the baseline QISKit-Aer simulation, the requested chunks are always copied from CPU to GPU. That is, in the example above, the CPU copies $\text{chunk}_3$ to GPU. After the $\text{chunk}_3$ is updated together with $\text{chunk}_1$, it is copied back to the CPU memory.

Note that, as the GPU memory capacity is much less compared to the CPU host memory, a large number of chunks are statically allocated on CPU memory when the number of qubits is large. For instance, on the P100 GPU with 16 GB memory, we observe from experiments that when simulating a circuit that has 34 qubits, the state vector is divided into 8192 chunks, 496 chunks are allocated on GPU, while the remaining 7696 chunks are all on CPU. Therefore, one can expect that most of the time, the CPU does the state amplitude update without benefiting from the GPU acceleration.

![Figure 28](image-url)

Figure 28: Example of baseline execution where the state vector is statically partitioned and allocated on CPU and GPU.

### A.1.4.3 Characterization and Observations

In this section, we quantify the simulation performance of the baseline QISKit-Aer. We first study the scalability when the number of qubits increases. We observe that, if there are less than 30 qubits in the circuit, the baseline GPU simulates much faster than compared CPU-based simulation
(e.g. 9.67× speedup for 29-qubit circuits on average), since the entire state vector fits in the P100 GPU memory and there is no need for data exchange and synchronization. However, the baseline GPU performance significantly drops when the number of qubits is larger than 30. It becomes even worse than running on the CPU alone when the number of qubits reaches 32. In particular, we observe a factor of 1.8× slowdown for qft_33 as an example.

![Graph showing baseline execution time breakdown.](image)

Figure 29: Baseline execution time breakdown.

To investigate the reason for this slowdown, we show the breakdown of the execution time in Figure 29. One can observe that, on average, 89.34% of the execution is spent on the CPU, indicating that the GPUs are not properly used in the baseline execution for large number qubit circuits. Moreover, the overheads involve amplitude exchange and synchronization occupies 9.91% of the average execution time, and the computation time of GPU only occupies 0.71% of total time on average. In other words, most of the computation is performed by the CPU and the GPU is idle due to the static state chunk allocation in the baseline GPU execution. In Figure 33, 🅜 depicts the execution timeline of the baseline.

**A.1.4.4 Will a Naive Optimization Work?**

To improve the GPU utilization during simulation, an intuitive optimization would dynamically allocate the chunks and transfer the chunks to GPU for updates. In this section, we investigate whether the naive implementation works well or not.

We implemented the dynamic state vector chunk allocation in QISKit-Aer. Figure 30 depicts the execution time of the naive optimization normalized to the baseline execution. Surprisingly, none of the quantum circuits we studied show improvements when using dynamic allocation. To

\[ \text{In this paper, we use } n \text{ in the circuit name (e.g., cir_n) to represent a circuit with } n \text{ qubits.} \]
Figure 30: Normalized execution time of naive approach.

Figure 31: Execution time breakdown of naive optimization.

further investigate the reason, we break down the execution time and show the results in Figure 31. As can be seen from the figure, while CPU execution time significantly reduces and the data movement dominates, indicating that the GPU is waiting for data most of the time during execution. Therefore, naive dynamic allocation alone does not work to deliver good QCS performance. More sophisticated end-to-end optimizations are required to systematically improve the QCS performance and scalability.

### A.1.5 Q-GPU

In this paper, we propose Q-GPU, a framework that features several end-to-end optimizations. Figure 32 depicts the high-level overview of Q-GPU. (1) Q-GPU performs proactive state amplitude transfer to fully utilize the bi-directional data transfer bandwidth between CPU and GPU (Section A.1.5.1). (2) Before copying state amplitudes to GPU, Q-GPU performs dynamic redundancy elimination that prunes zero state amplitudes to avoid unnecessary data movements (Section A.1.5.2). (3) Q-GPU features a compiler-assisted, dependency-aware quantum gate reordering
to enlarge the potential of pruning (i.e., the number of zero amplitudes). Q-GPU implements a GPU-supported, lossless amplitude compression to further reduce the data transfer caused by non-zero state amplitudes with minimal runtime overheads (Section A.1.5.4).

A.1.5.1 Proactive State Amplitudes Transfer

In the naive execution, one reason behind the poor GPU utilization is the sequential state amplitude transfer between CPU and GPU. Specifically, when the GPU finishes updating all local chunks, those chunks are first copied back to CPU memory before the CPU can transfer the next batch of un-updated chunks to the GPU. This restriction is reasonable in the scenarios when particular chunks are involved in consecutive updates since the chunks being copied from the GPU’s memory cannot be overwritten during the copying. In other words, data movements are synchronized to avoid data conflicts. However, if the subsequent chunks from the CPU are not copied to the same memory locations on the GPU where current chunks are stored, such data conflict does not exist. As a result, one can transfer the chunks simultaneously from the CPU to the GPU and from the GPU to the CPU.

In our work, Q-GPU leverages CUDA streams to enable concurrent and bi-directional chunk copy to fully utilize the available bandwidth between the CPU and GPU. To avoid potential data conflict, Q-GPU implements two CUDA streams and partitions the GPU memory into two halves. One stream is responsible for the first half partition that acts as a buffer holding the chunks the GPU
is currently updating. The other stream is responsible for the second half partition that acts as a buffer for “prefetching” the next chunks for the GPU to update. The two memory partitions work as “circular buffers” to feed the GPU with the required chunks. These two streams can potentially overlap and execute concurrently.

Figure 33 illustrates the timeline of the baseline and each of our optimizations. The proposed proactive state amplitude transfer (III) achieves $A$ cycles savings compared with the baseline (I). We also show that the naive approach (II) performs worse than the baseline.

Figure 33: Time-line graph showing the benefits of each optimization in Q-GPU.

A.1.5.2 Pruning Zero State Amplitudes

While overlapping improves the bandwidth utilization, the total amount of amplitudes that are transferred remains unchanged. To reduce the data movement, we observe that there exist a considerable amount of zero state amplitudes that do not need to be updated during simulation. Thus, those zero state amplitudes can be pruned before transferring the chunks.

**Source of zero amplitudes:** Let us assume there are $n$ qubits, the initial states are usually set as $|0\rangle^\otimes n$ in the general QCS, indicating that all qubits have zero probability of being measured as $|1\rangle$. Hence, all state amplitudes are zeros, except for $a_0|0_2\ldots0_m\rangle$ which is 1. As the state of a particular qubit is unchanged until an operation is being applied on it, its state remains $|0\rangle$ until that operation happens. For instance, if a particular qubit $q_k$ is $|0\rangle$, all the state amplitudes $a_{\ldots\ldots1_k\ldots\ldots}$ are zeros since $q_k$ has zero probability to be measured as $|1\rangle$. In general, if $m$ of $n$-qubits are not involved, amplitudes $a_{\ldots0_k\ldots0_k\ldots0_k\ldots}$ are possible to be non-zero values, whereas the remaining amplitudes
are guaranteed to be zero values, i.e. $2^n - 2^{n-m}$ amplitudes are zero values. Therefore, even if only one qubit is not involved, then half of the state amplitudes are zeros.

**Pruning potential:** To investigate the potential of pruning, Table 7 lists the number of total operations and the number of operations before all qubits are involved. For circuits like iqp, we can expect a significant reduction of data movement after pruning since many qubits are not involved until the end of execution. However, for qft and qf, all qubits are involved at the beginning of execution, diminishing the potential of pruning benefits. We also use hchain_18 as an example and plot the distribution of state amplitudes after each operation (i.e., quantum gate) being applied in a quantum circuit. Figure 34 shows the state amplitude distribution after 0, 30, 60 and 90 operations.

During simulation, the amplitudes are gradually updated to non-zero values since more qubits are involved.

Figure 34: State amplitudes distribution of hchain_18, after 0, 30, 60 and 90 operations from left to right. Blue and orange lines denote real and imaginary parts of an amplitude respectively.

In general, let us assume we have an operation involving $m$ states, if all of the states are zero, these $m$ states remain zeros after applying any operation. As a result, we do not need to transfer the zero state amplitudes to the GPU as their values will not change. Therefore, one can reduce the data movement between CPU and GPU by pruning the zero state amplitudes. One intuitive approach is to check each state value by traversing all states. However, a more efficient approach can be adopted, as we illustrate below.

**Pruning Mechanism:** In the proposed Q-GPU, we use bits in a binary string as flags to indicate whether a qubit has been involved after a set of gate operations (denoted as involvement in Algorithm 1). Initially, all the bits in involvement are set to 0. When $q_k$ is involved, the $k$th bit
Table 7: The number of total operations and the number of operations before all qubits are involved for all circuits with 34 qubits.

<table>
<thead>
<tr>
<th>Circuit</th>
<th>Total Operations</th>
<th>Operations Before Completely Involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>hchain</td>
<td>1786</td>
<td>272</td>
</tr>
<tr>
<td>rqc</td>
<td>124</td>
<td>54</td>
</tr>
<tr>
<td>qaoa</td>
<td>754</td>
<td>19</td>
</tr>
<tr>
<td>gs</td>
<td>37</td>
<td>16</td>
</tr>
<tr>
<td>hlf</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>qft</td>
<td>184</td>
<td>13</td>
</tr>
<tr>
<td>iqp</td>
<td>146</td>
<td>132</td>
</tr>
<tr>
<td>qf</td>
<td>222</td>
<td>16</td>
</tr>
</tbody>
</table>

in involvement is set to 1. Recall that the state vector is partitioned into chunks, the index of a chunk, i.e., iChunk, determines whether a chunk will be transferred or not. To compare iChunk with flag bits in involvement, we define iChunk' as the left-shifted iChunk to align with involvements. When iChunk' is larger than involvement, it indicates that at least one bit of iChunk' is 1 and the corresponding flag bit in involvement is 0. In this situation, the corresponding qubit (i.e., indexed by this flag bit) has not been involved by any operation. As such, we skip the remaining chunks and stop the iteration (line 5). On the other hand, if iChunk' is smaller than or equal to involvement, the redundancy within a chunk is determined by iChunk' & involvement (line 8). For a qubit whose corresponding bit in iChunk' is 1, if it has already been involved by previous operations, its corresponding bit in involvement is also 1. Therefore, for all the qubits that is 1 in iChunk', if all of them have already been involved by previous operations, iChunk' & involvement results in iChunk' itself. Otherwise, all the state amplitudes within this chunk are zeros, and we can prune this chunk. Moreover, the chunkSize here is dynamically determined rather than a statically fixed value, which enhances the benefit of the above-discussed strategy. Specifically, we select chunkSize by finding
the least non-zero bit of *involvement*. This is useful, especially at the beginning of the simulation where many state amplitudes are zeros. For instance, assuming we have an 8-qubit circuit and the *involvement* flag is 00000011 at the early execution stage, the *chunkSize* is dynamically set to 2, which has fewer zeros within a chunk compared to a larger chunk. The *involvement* flag bits are updated according to the qubits involved in each operation (line 14). In Figure 33, the proposed pruning mechanism (IV) further saves (B) cycle over (III).

**Algorithm 1:** Pruning zero state amplitudes.

**Variable list:**
- $N$: Total chunks number in CPU,
- *involvement*: Flag indicating which qubits are involved

```plaintext
1 /* Determine chunkSize by locating the least non-zero bit of involvement */
2 chunkSize, N = getChunkSize(involvement)
3 for iChunk ← 0 to N − 1 do
4   iChunk' = iChunk << chunkSize
5   if iChunk' > involvement then
6     break
7   if iChunk' & involvement ≠ iChunk' then
8     continue
9 /* Amplitudes update */
10 updateInvolvement(involvement)
```

**A.1.5.3 Reordering to Delay Qubit Involvement**

In order to enlarge the potential of pruning, such that more state amplitudes are zeros during simulation, we propose compiler-assisted, dependency-aware quantum operation reordering to delay the involvement of qubits. Specifically, when applying a gate, we choose the one that incurs the minimum number of additional qubits to be involved with those qubits that have been already involved by previous operations. For example, Figure 35a shows the gs_5 circuit in the original
Figure 35: A walk-through example to illustrate the reordering benefits using gs_5. The red number denotes the operation orders before and after reordering. 

The gates are executed in the order $H$ gates, where each gate applies to an individual qubit. As a result, once these gates have been applied, all the five qubits are involved. The next operation is a CNOT gate applied to qubits $q_0$ and $q_1$ ($CNOT_6$). All the state amplitudes are likely non-zero because the qubits are involved by the $H$ gates. Therefore, applying this CNOT gate requires updating all the non-zero amplitudes in the state vector, leading to moving and traversing the entire state vector on the GPU. However, the $CNOT_6$ can be executed before some of the $H$ gates without violating the circuit semantics. This gate reordering allows more zero state amplitudes (fewer data movements) when simulating the $CNOT_6$ gate. It is also important to emphasize that any reordering must ensure that the gate dependencies are presented. For instance, $CNOT_6$ and $CNOT_7$ cannot be reordered due to the dependency on $q_0$.

To this end, we propose a compiler-assisted optimization to reorder the gate sequence with the goal of delaying the qubit involvement. Specifically, gates that are applied on different qubits in a quantum circuit can be executed independently in any order and the execution sequence of these independent gates does not affect the final simulation result.\textsuperscript{221,244,261} This provides us the opportunity to reorder the independent gates, we use a directed acyclic graph (DAG) to represent the gate dependency in a circuit. Based on the DAG, we reorder the independent gates such that the simulation sequence involves the minimum number of new qubits when simulating each gate. Specifically, we investigate two heuristic strategies: 1) greedy reordering, and 2) forward-looking reordering.
Algorithm 2: Quantum operation reorder.

Input:  \(DAG\) A DAG representing circuit dependencies.

Output: \(gatesList\) List of gates after reordering.

1 \(gatesList = \left[ \right]\)
2 \(exeList = \left[ \right]\)
3 /* First we build \(DAG\) and push gates without predecessors to an
   execution list */
4 \textbf{for} \(g\) \textbf{in} \(DAG\) \textbf{do}
5 \hspace{1em} \textbf{if} \(g\).numPredecessors() == 0 \textbf{then}
6 \hspace{2em} exeList.append(\(g\))
7 /* Then we traverse \(DAG\) in topological order and greedily decides the
   execution order of the gates */
8 \textbf{while} \(exeList \neq \emptyset\) \textbf{do}
9 \hspace{1em} nextGate = NULL
10 \hspace{2em} minCost = 0
11 \hspace{2em} \textbf{for} \(g\) \textbf{in} \(exeList\) \textbf{do}
12 \hspace{3em} cost = \(g\).getCost()
13 \hspace{3em} \textbf{if} cost < minCost \textbf{then}
14 \hspace{4em} minCost = cost
15 \hspace{4em} nextGate = \(g\)
16 \hspace{2em} exeList.erase(nextGate)
17 \hspace{2em} gatesList.append(nextGate)
18 \hspace{2em} \textbf{for} \(g\) \textbf{in} nextGate.descendants() \textbf{do}
19 \hspace{3em} \(g\).numPredecessors() = \(g\).numPredecessors() - 1
20 \hspace{3em} \textbf{if} \(g\).numPredecessors() == 0 \textbf{then}
21 \hspace{4em} exeList.append(\(g\))
**Greedy reordering:** greedy reordering traverses the DAG in topological order and greedily selects the gate (i.e., node in the DAG) that introduces the minimum number of new qubits to the list of updated qubits. The details of this method are illustrated in Algorithm 2. First, gates without predecessors in the DAG can be executed at the first steps and are put into `exeList`. Second, we traverse the gates in `exeList` and find the one that introduces the minimum number of newly involved qubits (lines 13 to 19). Then, we remove this gate from `exeList` and append it to the list of re-ordered gates. Third, we traverse the descendants of this gate and if a descendant does not have any predecessors other than this current gate, it will be added to `exeList` (lines 22 to 27). The second and the third steps are repeated until `exeList` is empty. In the rest of this section, we use Figure 35a as the example to illustrate how we perform reordering. At first, the `exeList` is \([g_1, g_2, g_3, g_4, g_5]\). Since each of these five gates involves one new qubit, we randomly select one gate among them to start simulation. In this example, \(g_1\) is selected as the starting gate. After traversing all its descendants, no new gates can be added into `exeList`. Next, the `exeList` becomes \([g_2, g_3, g_4, g_5]\). In the next three steps, we randomly select \(g_3, g_5\) and \(g_2\) since no new gates can be executed and all gates in `exeList` have equal priority. Then the `exeList` becomes \([g_4, g_6]\). At this time, `involvedQubits` is \([q_0, q_1, q_2, q_4]\). Therefore, \(g_4\) involves one new qubit \((q_3)\), whereas \(g_6\) will not introduce any new qubits since it acts on \(q_0\) and \(q_1\) that are already in the involved list. Therefore, we will greedily select \(g_4\) to execute since it involves the least new qubits. One can follow these reordering steps to reach the new ordering shown in Figure 35b. As a result, the number of involved qubits at each step is \(1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 4 \rightarrow 4 \rightarrow 5 \rightarrow 5 \rightarrow 5\). Since the baseline is \(1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5 \rightarrow 5 \rightarrow 5 \rightarrow 5 \rightarrow 5\), the final involvement is delayed by two steps. However, a better solution for reordering is to select \(g_2\) and \(g_6\) in the second and the third step, since applying these two gates only adds one qubit to `exeList`, while applying \(g_3\) and \(g_5\) adds two. Thus greedy reordering may misses the optimal choice.
Algorithm 3: Cost calculation in forward-looking reordering.

**Input:**
- \textbf{g} Gates from \textit{exeList},
- \textit{exeList} List of gates that are executable,
- \textit{involvedQubits} Set of qubits which have already been acted on.

**Output:**
- cost Potential involved qubits after executing \textit{g}.

1. \texttt{costCurrent} = 0, \texttt{costLookAhead} = 0
2. /* First we compute additional qubits that will be acted on by executing current gate */
3. \textbf{for} \textit{q} \textbf{in} \textit{g}.\texttt{qubits()} \textbf{do}
4.     \textbf{if} \textit{q} \textbf{not} \textbf{in} \textit{involvedQubits} \textbf{then}
5.         \texttt{costCurrent} = \texttt{costCurrent} + 1
6.         \textit{involvedQubits}.\texttt{insert}(\textit{q})
7. \texttt{exeList}.\texttt{erase}(\textit{g})
8. \textbf{for} \textit{g'} \textbf{in} \textit{g}.\texttt{descendants()} \textbf{do}
9.     \textbf{if} \textit{g'}.\texttt{numPredecessors()} == 1 \textbf{then}
10.         \texttt{exeList}.\texttt{push}(\textit{g'})
11. /* Then we traverse current \textit{exeList} and compute the cost of selecting a gate that involve least additional qubits */
12. \textbf{for} \textit{g''} \textbf{in} \textit{exeList} \textbf{do}
13.     \texttt{curCostLookAhead} = 0
14. \textbf{for} \textit{q'} \textbf{in} \textit{g''}.\texttt{qubits()} \textbf{do}
15.     \textbf{if} \textit{q'} \textbf{not} \textbf{in} \textit{involvedQubits} \textbf{then}
16.         \texttt{curCostLookAhead} = \texttt{curCostLookAhead} + 1
17.     \textbf{if} \texttt{curCostLookAhead} < \texttt{costLookAhead} \textbf{then}
18.         \texttt{costLookAhead} = \texttt{curCostLookAhead}
19. \texttt{cost} = \texttt{costCurrent} + \texttt{costLookAhead}
20. \textbf{return} \texttt{cost}

**Forward-looking reordering:** To address the deficiency in greedy-reordering, we propose Forward-
looking reordering that looks ahead of all the equal-priority gate candidates before making a decision. We implemented a cost counter to determine the priority of the gates in \( \text{exeList} \). In greedy reordering, the cost is simply computed by counting new involved qubits (line 3-8 in Algorithm 3). The cost in forward-looking reordering is computed using Algorithm 3. Note that, \( \text{exeList} \) and \( \text{involvedQubits} \) are just copies of the original ones, thus their original values are not changed. In forward-looking reordering, the cost of selecting a gate in \( \text{exeList} \) consists of two components: \( \text{costCurrent} \) and \( \text{costLookAhead} \) (line 1). The \( \text{costCurrent} \) is the same with the cost used in greedy reordering. Let us still use the example in Figure 35a to illustrate Algorithm 3. Initially, the \( \text{exeList} \) is also \([g_1, g_2, g_3, g_4, g_5]\). We take \( g_1 \) as an example to explain the computation of \( \text{costLookAhead} \). First, we assume \( g_1 \) has already been executed. Then, the \( \text{costCurrent} \) is 1 and \( \text{involvedQubits} \) becomes \([q_0]\) (lines 3-8). Since no descendants of \( g_1 \) can be executed, the \( \text{exeList} \) becomes \([g_2, g_3, g_4, g_5]\) (lines 9-14). Then, we traverse the \( \text{exeList} \). For each gate in \( \text{exeList} \), we compute the cost of selecting this gate by counting the new involved qubits (lines 18-21) and selecting the least cost as \( \text{costLookAhead} \). Now, executing any gate in \( \text{exeList} \) will involve one new qubit, thus \( \text{costLookAhead} \) is computed as 1 (lines 16-26). Similarly, one can find that all gates at the first step have equal priority. For the purpose of illustration, we assume \( g_1 \) is randomly selected. Then the \( \text{exeList} \) becomes \([g_2, g_3, g_4, g_5]\). Although all gates still have equal \( \text{costCurrent} \), we can find that \( g_2 \) has the least \( \text{costLookAhead} \). The reason is that, when we assume executing \( g_2 \) and look ahead from \( g_2 \), we find that executing \( g_6 \) introduces no new qubits. In contrast, look ahead after executing other gates will introduce new qubits. Finally, we get the result of forward-looking reorder as shown in Figure 35c. Clearly, the involvement at each step become \( 1 \rightarrow 2 \rightarrow 2 \rightarrow 3 \rightarrow 3 \rightarrow 4 \rightarrow 4 \rightarrow 4 \rightarrow 5 \). Compared with greedy reordering, we further delay the final involvement by two steps.

![Figure 36: Qubit Involvement during simulation in three representative circuits.](image)
Reorder effectiveness: To assess the performance of the reordering algorithms discussed above, we implement them to reorder the original operation sequences for all benchmark circuits that have 22 qubits and plot the involvement (Algorithm 1 in Section A.1.5.2) after each gate has been applied. For the purpose of illustration, we depict the results of three representative benchmark circuits in Figure 36. For each order, i.e. original order, greedy-reorder, and forward-looking reorder, the “speed” of reaching the maximum involvement indicates the pruning potential. We observe that, forward-looking reordering results in the largest pruning potential, while greedy reordering only works for qft_22 and even results less pruning potential than baseline for gs_22. Particularly, for gs_22 and qft_22, forward-looking reordering effectively delays the involvement of qubits. Thus, we can expect the pruning potentials of these circuits to be enlarged by forward looking reordering. However, for qaoa_22, none of the reordering algorithms work due to the prevalent dependencies among the gates. Refering back to Figure 33, when reordering (⊝) is employed, we can prune more chunks, which saves additional cycles compared to (⊞).

A.1.5.4 Non-zero State Compression

Compressibility: While pruning removes the zero state amplitudes, those non-zero amplitudes still cause data movement overheads especially for circuits that do not have large pruning potentials (e.g., qaoa in Figure 36). Targeting reducing the data movement caused by non-zero state amplitudes, we investigate the potential compressibility and propose a GPU-supported efficient lossless data compression in Q-GPU. Specifically, we observe that many non-zero entries within a state vector, after each operation, have similar amplitude values. In other words, there is a significant “spatial” similarly among consecutive state amplitudes in the state vector. To demonstrate the compressibility, we use qaoa_20 and iqp_20 as examples and show the residuals by subtracting the consecutive state amplitudes. As one can observe from Figure 37, for qaoa_20, most of the residuals are zero or very close to zero, indicating a potential for residual-based compression. However, iqp will be less compressible due to more diverse distribution.

Compression Strategy: We use the GFC algorithm\textsuperscript{262} in Q-GPU. We implement the GFC as GPU kernels to perform the compression in parallel, thereby reducing the compression and decompression overheads. Specifically, the amplitudes on the GPU are partitioned into micro-chunks with a size
Figure 37: Residual distributions for qaoa\_20 and iqp\_20.

Figure 38: Overview of compression in Q-GPU.

of 32 amplitudes. Each GPU warp iteratively compresses/decompresses in parallel. Figure 38 (on the top) shows the compressed format. For the 32 values of a micro-chunk, we first store a 4-bit prefix for each of them, where one bit is used to record the sign of the residual and another three bits are a count of leading zero bytes of the residual. Figure 38 also illustrates the GPU support of compression and decompression in Q-GPU. The compression is performed on the GPU after updating the chunk before copying it to the CPU. All of the chunks are equally divided into “segments”. We empirically choose the segment size to match the GPU parallelism such that the GPU is properly utilized during compression. The compressed segments are transferred to the CPU instead of the original state chunks. The CPU keeps the compressed segments and copies the compressed segments to the GPUs upon request. Once the chunks are copied to the GPU, the amplitudes are decompressed, updated, and then compressed. As can be seen from Figure 33, compression (✓) saves $D$ cycles over (✗) and introduces negligible overhead. Later, in section
A.1.6, we quantify the overheads incurred by the compression and decompression procedures.

### A.1.6 Experimental Evaluation

In this section, we evaluate Q-GPU using the eight circuits in Table 6. We implement Q-GPU by substantially extending IBM QISKit-Aer. The evaluation is conducted on the same CPU-GPU platform used for characterization. For all experiments, the default optimizations in QISKit-Aer are turned on in both baseline and Q-GPU evaluation. To show the effectiveness of each optimization, we test six different versions of executions for all quantum circuit benchmarks:

- **Baseline:** This version is the implementation with state-of-the-art GPU support in QISKit-Aer that supports GPU acceleration. As illustrated in Section A.1.4.2, state amplitudes are statically allocated on the GPU and CPU in this version.
- **Naive:** This version is the intuitive implementation discussed in Section A.1.4.4, which dynamically allocates state amplitudes to GPU. The performance of this version is dominated by expensive data movements.
- **Overlap:** This version implements the first optimization – proactive state amplitude transfer – in Q-GPU. This version is built upon the *Naive* version and its details are discussed in Section A.1.5.1.
- **Pruning:** This version adds the proposed pruning mechanism (Section A.1.5.2) to *Overlap*. By skipping the data movement of zero state amplitudes, the amount of data movement is reduced.
- **Reorder:** In this version, we implement forward-looking reorder algorithm (Section A.1.5.3) to enlarge the potential for pruning. This reordering is performed by a simple compiler pass integrated in the Q-GPU.
- **Compression/Q-GPU:** In this version, all optimizations are employed with compression. We also call it *Q-GPU*. Compression (Section A.1.5.4) is added on top of *Reorder*. This version achieved the best performance.

#### A.1.6.1 Overall Performance

Figure 39 shows the overall performance and scalability among the six versions for all eight quantum circuits. The y-axis in the figure denotes the normalized execution time to the *Baseline*
version. From the figure, one can make the following observations. First, by adding the proposed optimization in Q-GPU, our approach significantly reduces the execution time of QCS across all the circuits. Specifically, Overlap, Pruning, Reorder, and Compression/Q-GPU see a 24.96%, 44.54%, 56.78%, and 71.66% execution time reduction over the baseline execution for the largest number of qubits that can run on our platform. Second, the scalability of QCS performances is significantly improved by “breaking” the memory capacity in Q-GPU. The average achieved performance outperforms baseline by $2.53 \times$ for 34 qubits. Although we only simulate up to 34 qubits due to the CPU memory limitation (384 GB) in our system (Section A.1.4.3), one can infer from the trend that our optimizations are scalable to larger sized circuits. Third, Q-GPU has different accelerations for different circuits. Specifically, for gs, qft, qaoa and iqp, higher execution time reduction is observed, whereas for hchain and rqc, less speedup is observed. This is because, for hchain and rqc, reordering cannot enlarge the pruning potential because of dependent gates. Their amplitude residuals also have disperse distribution (similar to iqp in Figure 37). Thus, either Reorder or Compression improves little for these two benchmarks. Finally, for different circuits, a certain version may not have the same acceleration effects. For example, Overlap version generates a similar execution time reduction in all circuits tested. However, for Pruning, Reorder and Compression, the runtime reduction is different between different circuits. For example, Pruning and Reorder improve little for qaoa and qf because these two circuits do not have much potential

Figure 39: Normalized simulation time for circuits with different number of qubits (the lower the better).
of pruning the zero amplitudes. That is, their qubits get involved quickly with dependent operations. However, qaoa achieves significant benefits by compression as the great potential of compressibility. (discussed in Section A.1.5.4).

![Figure 40: Normalized data transfer time (lower the better).](image)

To further understand the execution reduction, Figure 40 plots, for each version, the exposed data movement time. In this figure, the y-axis represents the data movement time normalized to the Naive version. Clearly, one can observe a step-wise data movement reduction in the versions with our optimizations. First, Overlap uniformly reduces the data transfer time by an average of 46.14%. Note that, the savings generated in Overlap are independent of circuit types, that is the reason behind execution time reduction in Figure 39. For Pruning and Reorder, the reduction of data movement time varies in different circuits. This is because the number of zero state amplitudes and the potential of pruning heavily rely on the circuit type. For example, qaoa, qft, and qf get all qubits involved at early stage of simulation. Hence, pruning is less effective for these circuits compared to others. Also, as discussed in Section A.1.5.3, Reorder has little effects on hchain, rqc, qaoa, and qf due to dependent operations in these circuits. Therefore, Reorder delivers similar data transfer time reduction with Pruning for these circuits. However, for those circuits with less dependent operations, Reorder significantly reduces their data movement time by enlarging the pruning potential. For circuits like qaoa, gs, qft and qf, Compression effectively reduces the data movement by leveraging the spatial similarity discussed in Section A.1.5.4. In a nutshell, for all circuit benchmarks tested, the reductions of data transfer time are the main reason behind the execution time reduction in Figure 39.

We also quantify the computation time of compression and decompression in Figure 41. Overall, the compression and decompression overhead is 3.12% and 2.74% of the GPU execution time. Potentially one may further optimize the compression and decompression by overlapping them on
GPU, but we found the overhead is negligible compared to the significant reduction in execution time that we achieved. We also want to emphasize that the execution times reported in Figure 39 have all the sources of overhead included.

![Figure 41: Compression and decompression overheads.](image)

**A.1.6.2 Comparison with OpenMP**

Many publicly available quantum simulators and existing works employ OpenMP to parallelize the QCS on CPUs.\textsuperscript{221,228,240} We compare Q-GPU with these OpenMP implementations. Specifically, we chose the OpenMP implementation in the most recent QISKit simulator and plot the results in Figure 42. We also compared our approach with other simulators in the next section, where the OpenMP is used by default in the simulators. On average, across eight circuits, Q-GPU outperforms the OpenMP QISKit by 1.79×. Particularly, Q-GPU achieved 12.79× speedup in qft. For $g_8$, $iqp$ and $qf$, Q-GPU achieves more than 2× speedup. However, for $hchain$ and $rqc$, Q-GPU performs worse than OpenMP. This is because the pruning potential and the compressibility are low in both circuits where Q-GPU is less effective.

![Figure 42: Comparison with OpenMP.](image)
A.1.6.3 Comparison with Other Simulators

We compare Q-GPU with other simulators, including Google Qsim-Cirq v0.8.0 plus Cirq v0.9.2 and Microsoft QDK v0.15. In our experiments, we run these simulators on the same CPU (Section A.1.4.2). Note that, both Qsim-Cirq and QDK are OpenMP enabled and we observe that they used all available threads during execution on the CPU. We report the results in Figure 43.

It is important to note that, to enable the simulation of the same circuits on Qsim-Cirq, we need to first transform our circuit benchmarks into OpenQASM codes. Then, we need to import the OpenQASM codes to Qsim-Cirq for execution. Unfortunately, not all the transformed circuits can be simulated on Qsim-Cirq due to the lack of support for particular gates (i.e., the “cp” gate cannot be recognized by Qsim-Cirq). As a result, we can only run gs and hlf successfully. This motivates our future research on uniform support of Quantum programming models. Figure 43a shows the normalized speedup of the proposed Q-GPU compared to Qsim-Cirq. Q-GPU outperforms the Google Qsim-Cirq by $1.02 \times$ on average.

To run the same quantum circuit on Microsoft QDK v0.15, we have to further convert the OpenQASM codes to “qsharp”, i.e., the quantum language used in Microsoft. The conversion only succeeded for qft, iqp, hlf, and gs. The normalized simulation time is plotted in Figure 43b. On average, Q-GPU performs $9.82 \times$ better than Microsoft QDK.
A.1.7 Related Works

To the best of our knowledge, Q-GPU is the first work that systematically optimizes quantum circuit simulation on a GPUs. We summarize the related prior efforts below.

Prior works have focused on QCS optimizations on different platforms, from readily available devices to cloud environments. Thomas et al. simulated 45-qubits circuit using 8,192 nodes. They optimized single node performance by using automatic code generation and optimization of compute kernels. Edwin et al. claimed to simulate more than 49 qubits by partitioning quantum circuits to “subcircuits” and delay their entanglements. In, the authors proposed lossy data compression to reduce the memory requirement of simulating large-scale quantum circuits. Aneeqa et al. focused on fully exploiting single CPU performance for simulating a large number of qubits. The developed algorithm aims to reorder circuits such that more gates can be simulated in parallel. Compared with all these efforts, Q-GPU takes advantage of GPUs while managing the data movement between CPU and GPU. First, we identify the source of zero state amplitudes in QCS, and propose a pruning mechanism to safely reduce unnecessary computation on these states, which saves not only computation but also data movement. Unlike prior works using reordering to aggregate gates, we propose reordering algorithms to enlarge the pruning potential. Moreover, Q-GPU is the first framework that leverages the GPU to implement a lossless compression that does not affect accuracy of QCS. Finally, it is important to emphasize that Q-GPU is complementary to existing cloud-based quantum simulation frameworks, and can be integrated within these frameworks for further QCS improvements.

There are also several works that utilize GPUs to accelerate QCS. Most of these works have limited capability in simulating large quantum circuits due to the limited memory capacity of GPUs. Ang et al. proposed a multi-GPU centric QCS framework that tracks the density matrix. However, their framework cannot simulate a large number of qubits since it is limited by the aggregated memory capacity of multi-GPUs. For a single-node, they can only simulate up to 14 qubits on an NVIDIA V100 GPU. Jun et al. proposed a CPU-GPU co-simulation method that enables simulation using a GPU even when the required memory exceeds the GPU memory capacity. Their method is also integrated into the IBM QISKit and is used as the baseline in this paper. In summary, compared to prior work, Q-GPU breaks the GPU memory capacity limitation,
i.e., it is able to simulate 34 qubits which require 256 GB memory on a 16 GB memory GPU, and fully takes advantage of GPU parallelization. The fundamental design innovation behind this is to dynamically and proactively transfer the state amplitudes through end-to-end optimizations to minimize the data movement overheads caused by state amplitudes transfer.

A.1.8 Concluding Remarks

In this paper, we propose Q-GPU, a framework tailored with GPU optimizations to effectively improve the quantum circuit simulation performance for quantum circuits with a large number of qubits. The Q-GPU is able to deliver scalable simulation performance based on the four internal end-to-end optimizations, including i) proactive state amplitudes transfer, ii) zero state amplitudes pruning, iii) delayed qubit involvement, and iv) lossless non-zero state compression. Experimental results across eight representative quantum circuits indicate that Q-GPU achieves $2.53 \times$ average execution time reduction on a single GPU. It also outperforms the most recent OpenMP CPU implementation and other publicly available quantum simulators.
Appendix B Supporting Information for Chapter 4

In this document we provide a brief description of the methods used to calculate the atom centered multipoles and electrostatic potential scans reported in the main manuscript. For those interested in reproducing this work we include example inputs for the calculations at the GitHub repo: https://github.com/KidA3995/graphenes_quadrupole.git. In addition, we include the molecular coordinates for the PAHs as xyz files and the scripts used for plotting the results as Jupyter Notebooks.269

B.1 A Brief Note on Convention

We impose the traceless convention of Buckingham270,271 on all multipoles above the dipole. To demonstrate how the traceless condition is imposed we use the quadrupole moment in the Cartesian representation as an example,

\[ Q_{ij} = \frac{(3\langle ij \rangle - \text{Tr}[\langle ij \rangle] \delta_{ij})/2}{2} \]  \hspace{1cm} (80)

where \( i \) and \( j \) refer to the Cartesian components \((x,y,z)\) of the quadrupole moment. The angled bracket \( \langle ... \rangle \) indicates that the components of the quadrupole matrix are primitive, while \( Q_{ij} \) represents the traceless quadrupole moment matrix. The term \( \text{Tr}[\langle ij \rangle] \) is the trace of the primitive quadrupole matrix. The factor \( \delta_{ij} \) is the Kronecker delta,

\[ \delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases} \] \hspace{1cm} (81)

which ensures that the trace is only subtracted from the diagonal of \( \langle ij \rangle \). Putting equation 80 in matrix form we have the following,

\[ Q_{ij} = \begin{bmatrix} \frac{3\langle xx \rangle - ((xx)+(yy)+(zz))}{2} & \frac{3\langle xy \rangle}{2} & \frac{3\langle xz \rangle}{2} \\ \frac{3\langle xy \rangle}{2} & \frac{3\langle yy \rangle - ((xx)+(yy)+(zz))}{2} & \frac{3\langle yz \rangle}{2} \\ \frac{3\langle xz \rangle}{2} & \frac{3\langle yz \rangle}{2} & \frac{3\langle zz \rangle - ((xx)+(yy)+(zz))}{2} \end{bmatrix} \] \hspace{1cm} (82)

where we have substituted in the Cartesian components, expanded \( \text{Tr}[\langle ij \rangle] \), and distributed the factors of 3 and 1/2. One can see that \( \text{Tr}[Q_{ij}] = \sum_i Q_{ii} = 0 \), hence the name, “traceless.” We employ
an equivalent definition of tracelessness to obtain the primitive out-of-plane quadrupole ($\langle zz \rangle$) component in the main manuscript,

$$Q_{ij} = \frac{(3\langle ij \rangle - \langle r^2 \rangle \delta_{ij})}{2} \quad (83)$$

where $\langle (r)^2 \rangle$ is the spherical average of radius squared and all other terms are defined above. Equations 80 and 83 generalize to higher order multipoles (e.g. for the traceless octupole $\text{Tr}[Q_{ijk}] = \sum_i Q_{iii} = 0$) and we refer readers who are interested in seeing more to the relevant references.\textsuperscript{270,271}

**B.2 Methods: Calculating GDMA and BS-ISA Multipoles**

BS-ISA\textsuperscript{64,272} and GDMA\textsuperscript{39,273,274} multipoles reported in this work were calculated using the following process:

1. We asymptotically correct the exchange-correlation (XC) potential of PBE0.\textsuperscript{34,36} This requires knowing both the first ionization potential (IP) and energy of the highest occupied molecular orbital (HOMO). First, we calculate the IP of the molecule using the domain-based local pair natural orbital (DLPNO) version of equation of motion (EOM) coupled cluster theory with single and double excitations (CCSD) for ionization potentials (IP-EOM-DLPNO-CCSD)\textsuperscript{114,275} as implemented in ORCA v.4.2.0.\textsuperscript{276}

   a. A restricted Hartree-Fock (RHF)\textsuperscript{106–108} reference wavefunction is used for IP-EOM-DLPNO-CCSD. The orbital basis used is cc-pVTZ\textsuperscript{37} and the v e r y t i g h t s c f command is used to set the convergence criteria. For C$_{96}$H$_{24}$, we employ the RIJCOSX approximation where the Coulomb integrals are density fit (RI-J) and the exchange integrals are estimated semi-numerically via the, “chain-of-spheres,” approximation (COSX).\textsuperscript{277,278} For density fitting the Coulomb integrals we employ the def2-universal Coulomb fitting basis.\textsuperscript{279}

   b. To reduce the cost of obtaining the IP, IP-EOM-DLPNO-CCSD uses DLPNO to transform the integrals of CCSD from their canonical molecular orbital form to local pair natural orbitals (LPNOs), which essentially reduces the number of occupied and virtual orbitals that are used in the CCSD and EOM calculations.\textsuperscript{276} We use the n o r m a l P N O setting in ORCA, but reduce by an order of magnitude the threshold that determines the pairs to be treated via CCSD T C u t P a i r s = 1 e ^ { - 5} . We found that these settings afford a reasonable compromise
between accuracy and expense for \( \text{C}_{96}\text{H}_{24} \). In performing the DLPNO transformation the resolution of identity (RI) approximation is employed\(^{280}\) using the cc-pVTZ-RI fitting basis.\(^{281}\)

2. Next, we calculate the HOMO energy of the molecule using the density fitted PBE0 implemented in Psi4 v.1.4a2.dev213\(^{128–130}\) in the basis that will be used to calculate the multipole moments. The density fitted SCF in this step and the following step employ Coulomb-exchange (JK) fitting bases.

3. Calculate the multipole moments using a development version of CamCASP v.7.2.2\(^{264,272}\) interfaced to Psi4 v.1.4a2.dev213.
   a. The IP and HOMO energy determined in the two previous steps are used to asymptotically correct the the XC potential of PBE0 via the gradient regulated asymptotic correction (GRAC)\(^{159}\) method implemented in Psi4. The PBE0(AC) calculations used an energy convergence cutoff of \( \text{e}_{\text{convergence}} = 1 \times 10^{-11} \) a.u. and integrals with a value of \( \text{ints}_{\text{tolerance}} < 1 \times 10^{-10} \) were dropped. Otherwise, the default convergence/screening settings of Psi4 were used. The resulting molecular orbitals and electronic density were passed to CamCASP as a formatted checkpoint file to determine BS-ISA and GDMA multipoles.
   b. For GDMA, the multipoles were determined directly from the density matrix and orbitals from the Psi4 calculation.
   c. BS-ISA is a hybrid real-basis space extension of Lillstolen and Wheatley’s ISA method.\(^{59}\)

In BS-ISA, all the quantities that appear in the Stockholder equations (molecular density, atomic densities, and shape functions) are expanded in auxiliary bases. In this work, the atomic densities are expanded in RI fitting basis sets that have the s-block replaced with the ISA set2 s-functions developed by Misquitta, Stone, and Fazeli.\(^{64}\) The shape functions, which are also referred to as proatomic densities in the literature, are fit using only the ISA set2 s-function basis. The results reported in the main document make use of a custom basis we developed for fitting the molecular density. However, we did try fitting the molecular density with RI fitting basis sets and the ISA set2 s-function basis as well. The combinations of orbital and auxiliary bases we tested are shown in Table 8 and the details of why we developed a new fitting basis for the molecular density are in the text.

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following the table. We use the, “ISA-A,” algorithm to partition the molecular density into atomic domains and the atomic multipole moments are calculated using real-space grids (referred to as ISA-GRID moments in the literature\textsuperscript{272}). Adjustments were made to the real-space grids and algorithmic convergence parameters of this method. The details of these refinements will be discussed in an upcoming publication by the developers of the CamCASP package. We encourage the reader to review the relevant citations\textsuperscript{64,272} and look at the example input we provide in the GitHub repo, which contains the custom basis we developed as well.

A variety of orbital and fitting basis set combinations were tested in steps 2 and 3 of the above list to assess the sensitivity of the atomic multipoles. In Table 8 we tabulate all combinations.

Table 8: Various bases tested in the density fitted SCF calculation and calculation of atomic multipole moments.

<table>
<thead>
<tr>
<th>Shorthand</th>
<th>Orbital</th>
<th>SCF-Auxiliary\textsuperscript{a}</th>
<th>Molecular-Auxiliary\textsuperscript{b}</th>
<th>Atom-Auxiliary\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>aDZ/aDZ/aDZ\textsuperscript{d}</td>
<td>aug-cc-pVDZ</td>
<td>aug-cc-pVDZ-JKfit</td>
<td>aug-cc-pVDZ-RIfit + set2\textsuperscript{e}</td>
<td>aug-cc-pVDZ-RIfit + set2</td>
</tr>
<tr>
<td>aDZ/aDZ/aTZ</td>
<td>aug-cc-pVDZ</td>
<td>aug-cc-pVDZ-JKfit</td>
<td>aug-cc-pVDZ-RIfit + set2</td>
<td>aug-cc-pVTZ-RIfit + set2</td>
</tr>
<tr>
<td>aTZ/aTZ/aTZ</td>
<td>aug-cc-pVTZ</td>
<td>aug-cc-pVTZ-JKfit</td>
<td>aug-cc-pVTZ-RIfit + set2</td>
<td>aug-cc-pVTZ-RIfit + set2</td>
</tr>
<tr>
<td>aTZ/aTZ/aQZ</td>
<td>aug-cc-pVTZ</td>
<td>aug-cc-pVTZ-JKfit</td>
<td>aug-cc-pVTZ-RIfit + set2</td>
<td>aug-cc-pVQZ-RIfit + set2</td>
</tr>
<tr>
<td>aTZ/Pitt-fit/aQZ</td>
<td>aug-cc-pVTZ</td>
<td>aug-cc-pVTZ-JKfit</td>
<td>Pitt-fit\textsuperscript{f}</td>
<td>aug-cc-pVQZ-RIfit + set2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Basis used to density fit the SCF calculation.
\textsuperscript{b} Basis used to expand the molecular density in BS-ISA algorithm.
\textsuperscript{c} Basis used to expand the AIM densities are expanded in BS-ISA.
\textsuperscript{d} Shorthand designation of the basis sets used in this text.
\textsuperscript{e} + set2 indicates that the ISA set2 basis replaces the s-block of the RIfit basis.
\textsuperscript{f} A custom basis we developed. See text for more information.

The orbital bases are of the aug-cc-pVXZ family,\textsuperscript{37,38,282} the SCF-Auxiliary bases used for density fitting are of the cc-pVXZ Coulomb-exchange fitting (-JK) family with diffuse functions added.\textsuperscript{283} Note that the short hand basis notation in Table 8 applies only to BS-ISA as it includes the auxiliary basis sets. Only the orbital basis is used in GDMA, so only one entry will appear in its short hand (e.g. The aTZ/aTZ/aTZ, aTZ/aTZ/aQZ, and aTZ/Pitt-fit/aQZ calculations for BS-ISA will all be notated as aTZ for GDMA.)

As noted previously, BS-ISA makes use of extensive density fitting. Initially, we fit both the molecular PBE0(AC) density ($\rho(\mathbf{r})$) and atomic densities $\rho^a(\mathbf{r})$ in CamCASP with the aug-cc-pVXZ-RI bases\textsuperscript{281} with their s-block replaced by the ISA set2 s-function basis.\textsuperscript{64} However, the
model ESP of the BS-ISA moments at the aTZ/aTZ/aQZ level incurred appreciable error relative to the reference ESP of PBE0(AC) even when atomic hexadecapoles were included in the multipole expansion. We found that the primary source of this error stemmed from insufficient higher order angular momenta blocks of the Molecular-Auxiliary basis. To address this, we developed a Molecular-Auxiliary basis (notated to as, “Pitt-fit,” here and in the main document) which has two more p functions and one more d function for carbon than aug-cc-pVTZ-RI. Additionally, there is one more p, d, and f function for hydrogen than aug-cc-pVTZ-RI. As noted previously, in all our calculations the s-block of the Molecular-Auxiliary basis (aug-cc-pVTZ-RI in this case) is replaced by the ISA set2 basis. The Pitt-fit basis has two less s-functions for hydrogen than ISA set2 and one extra function for carbon. The exponents of the s-functions in our Pitt-fit basis are similar to that of ISA set2 and the exponents of the higher order angular momenta blocks are comparable to aug-cc-pVTZ-RI. However they are not exactly the same and for those interested the Pitt-fit basis set is available in the GitHub repo: https://github.com/KidA3995/graphenes_quadrupole.git.

The atomic moments reported in the main manuscript were obtained using PBE0(AC)/aTZ/Pitt-fit/aQZ calculations. However, we wanted to report the sensitivity of the $Q_{20}^C$ quadrupole component to the orbital and fitting bases, so there is data tabulated in this document for the four other combinations listed in Table 8.

B.3 Methods: Electrostatic Interaction Scans

In the main document, figure 15a plots the electrostatic interaction of a negative point charge with $C_{96}H_{24}$ when it is scanned along the C$_6$ rotational axis of the PAH. The figures plot energies for the interaction of the point charge with the PBE0(AC) charge density of $C_{96}H_{24}$ as well as the GDMA and BS-ISA multipoles parsed from that same charge density. The process for generating the data for these images went as follows:

1. Run a PBE0(AC) calculation in the basis used to generate the multipoles (aTZ orbital basis with the aTZ-JK SCF-Auxiliary basis). The steps involved in this calculation were detailed in steps 1, 2, and 3(a) of the section titled, “Methods: Calculating GDMA and BS-ISA Multipoles”.
2. Calculate the electrostatic interaction with the converged all-electron density on a grid of points.
running along the C\textsubscript{6} rotational axis of the PAH (z-axis in our geometry) with a step size of Δz = 0.2 using the grid\_esp feature of the one-electron properties, oeprop, module in Psi4 v.1.4a2.dev213.

3. Calculate the electrostatic interaction with GDMA and BS-ISA multipoles along the same grid using the program ORIENT v.5.0.08.\textsuperscript{284} This step was performed using a successively higher rank multipole expansion on the atoms using the `limit` command in ORIENT.

To generate the energy difference (ΔE\textsubscript{1es}\textsuperscript{1}) plot (figure 15b in the main document) we calculate the difference between the PBE0(AC) energy, E\textsubscript{1es}\textsuperscript{1}(PBE0(AC)), and that of the model multipolar energy, E\textsubscript{1es}\textsuperscript{1}(ℓ),

\[
ΔE\textsubscript{1es}\textsuperscript{1} = E\textsubscript{1es}\textsuperscript{1}(PBE0(AC)) - E\textsubscript{1es}\textsuperscript{1}(ℓ)\quad ℓ = 2, 3, 4
\]

In figure 15c of the main document we plot charge penetration estimates at small point charge-PAH separations (z ∼ 2 – 4), as the natural log of the absolute value of ΔE\textsubscript{1es}\textsuperscript{1}. These results are discussed in detail in the main document, so we only add here that the short-range curves were fit with linear functions using the `curve_fit` function of the python library SciPy.\textsuperscript{135}

As for the results where we evaluate the impact of edge dipoles on E\textsubscript{1es}\textsuperscript{1} between a negative point charge and increasingly large carbon nanoflakes (Figure 2 in the main document) two separate calculations were performed. For the results obtained without any edge dipoles the process went as follows:

1. Calculate the average atomic \(Q_{20}^C\) from the central six carbon atoms of C\textsubscript{24}H\textsubscript{12}, C\textsubscript{54}H\textsubscript{18}, and C\textsubscript{96}H\textsubscript{24} given by a BS-ISA calculation on PBE0(AC)/aTZ/Pitt-fit/aQZ density. The \(Q_{20}^C\) from C\textsubscript{54}H\textsubscript{18} and C\textsubscript{96}H\textsubscript{24} are our best estimate of graphene’s out-of-plane quadrupole, \(Q_{20} = -0.006\) a.u.. For systems larger than C\textsubscript{96}H\textsubscript{24}, we presume this converged \(Q_{20}^C\) value is representative of their out-of-plane quadrupole.

2. Generate a moments file for every hexagonal carbon nanoflake in the series C\textsubscript{6n}2 n = 2, 3, ..., 50 where \(Q_{20}^C\) is placed on every atom and all other moments are omitted.

3. For every carbon nanoflake, read in the moments file into ORIENT v.5.0.08\textsuperscript{284} and calculate E\textsubscript{1es}\textsuperscript{1} for the nanoflake and a negative point charge.

The process to generate results where both the atomic out-of-plane quadrupole \(Q_{20}^C\) and edge dipoles (\(Q_{1m}^{CH}\)) are present went as follows:
1. Construct \( Q_{1m}^{CH} \) for \( C_{24}, C_{54}, \) and \( C_{96} \) such that the combination of \( Q_{20}^{C} \) on every carbon atom and \( Q_{1m}^{CH} \) on only the edge carbon atoms of the nanoflakes reproduce the molecular out-of-plane quadrupole of the PAHs \( C_{24}H_{12}, C_{54}H_{18}, \) and \( C_{96}H_{24} \) when the \( \ell = 2 \) expansion (atomic charges, dipoles, and quadrupoles) of BS-ISA is used.

2. Plot the edge dipole magnitude of \( C_{24}, C_{54}, \) and \( C_{96} \) as a function of \( 1/r \) where \( r \) is the average distance of an edge carbon from the center of mass of the PAHs (determined using a nearest-neighbors algorithm).

3. Fit the function \( Q_{1m}^{CH}(1/r) = a \times (1/r) + b \) to the data using the Python library NumPy’s `polyfit` function and extrapolate to obtain edge dipole magnitudes for the hexagonal carbon nanoflakes in the series \( C_{6n^2} \) \( n = 2, 3, \ldots, 50 \). Figure 44 plots the results of the extrapolation procedure and the edge dipoles we constructed.

![Figure 44: Plot of model edge dipole magnitudes \( Q_{1m}^{CH} \) as a function of \( 1/r \) where \( r \) is the average radius of a nanoflake. The blue points are the edge dipoles we constructed to reproduce the molecular out-of-plane quadrupole component of PAHs \( C_{24}H_{12}, C_{54}H_{18}, \) and \( C_{96}H_{24} \). The function \( Q_{1m}^{CH}(1/r) \) was fit to the blue points and the orange points are the model edge dipoles extracted from the function.](image)

4. Generate a moments file for the hexagonal carbon nanoflakes \( C_{6n^2} \) \( n = 2, 3, \ldots, 50 \) where \( Q_{20}^{C} \) is
placed on every atom and the edge dipoles determined in the previous step are applied to the edge carbon atoms with the correct orientation. In this context, “correct orientation,” refers to the fact that the edge bond dipoles from BS-ISA point along the C-H bond towards the position of where a hydrogen atom would be in a PAH of the same size.

5. For each carbon nanoflake considered, read in the moments file into ORIENT v.5.0.08\textsuperscript{284} and calculate $E_{\text{ces}}^1$ for the nanoflake and a negative point charge.

The scripts used to calculate the average edge dipole, to calculate the average distance of an edge carbon in a PAH and nanoflake, and plot the ESP scan can all be found as Jupyter Notebooks in the GitHub repository.

\subsection*{B.4 Methods: Periodic Boundary Conditions}

We used the Castep\textsuperscript{171} code to perform periodic boundary condition plane-wave DFT calculations on graphene. A two-atom unit cell was employed, with a large extent of vacuum in the direction perpendicular to the sheet so as to minimise unwanted interactions between the sheet and its periodic images. The extent of the cell perpendicular to the sheet was 14\AA, and we tested convergence for this parameter by reducing it to 12\AA and increasing to 16\AA, which had negligible effect on the result. A 7x7x2 k-space sampling grid was used for most calculations, with convergence checked by increasing this to 9x9x2 and 11x11x2. A lattice parameter of just over 4.644 a.u. was used, and relaxation was not permitted. This approximation was justified by permitting relaxation for one calculation, which resulted in the lattice parameter increasing to 4.658 a.u. The component of the quadrupole moment of interest changed from -3.922 a.u. to -3.906 a.u. per atom.

Castep’s automatically-generated pseudopotentials were employed, and we used the LDA,\textsuperscript{172} PW91,\textsuperscript{173} PBE,\textsuperscript{33,35} and PBE0\textsuperscript{34,36} functionals. Both norm-conserving\textsuperscript{174} and ultra-soft\textsuperscript{286} pseudopotentials were used. All produced very similar results for the $\langle zz^a \rangle$ component of the quadrupole moment, ranging from -3.922 a.u. to -3.9510 a.u. per atom.
### B.5 Results: Multipole Moments

Table 9: Average charge and dipole magnitude on symmetry equivalent atom sets \((C_1, C_2, \ldots, H_{\text{dcc}2})\) in PAHs \(C_{6n}H_{6n}\) \(n = 1 \rightarrow 4\). Symmetry equivalent sets of hydrogen atoms on PAHs are designated by their subscripts: \(b \rightarrow \text{benzene}, c \rightarrow \text{coronene}, cc# \rightarrow \text{circumcoronene},\) and \(\text{dcc}\# \rightarrow \text{dicircumcoronene}\. All multipoles are spherical, traceless, and in atomic units.

<table>
<thead>
<tr>
<th>Atom</th>
<th>ISA-GRID aTZ/Pitt-fit/aQZ</th>
<th>GDMA aTZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q^a)</td>
<td>(\mu^a)</td>
</tr>
<tr>
<td></td>
<td>(C_6H_6)</td>
<td>(C_{24}H_{12})</td>
</tr>
<tr>
<td>(C_1)</td>
<td>-0.126</td>
<td>-0.001</td>
</tr>
<tr>
<td>(C_2)</td>
<td>0.125</td>
<td>-0.007</td>
</tr>
<tr>
<td>(C_3)</td>
<td>-0.198</td>
<td>-0.006</td>
</tr>
<tr>
<td>(C_4)</td>
<td>0.151</td>
<td>-0.006</td>
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<td>(C_5)</td>
<td>-0.302</td>
<td>-0.003</td>
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<tr>
<td>(C_6)</td>
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<td>-0.006</td>
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<tr>
<td>(C_7)</td>
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<td>0.000</td>
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<tr>
<td>(C_8)</td>
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<td>0.000</td>
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<tr>
<td>(C_9)</td>
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<td>0.000</td>
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<tr>
<td>(C_{10})</td>
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<td>0.000</td>
</tr>
<tr>
<td>(H_b)</td>
<td>0.126</td>
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<tr>
<td>(H_c)</td>
<td>0.136</td>
<td>0.000</td>
</tr>
<tr>
<td>(H_{cc1})</td>
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<td>(H_{cc2})</td>
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<td>(H_{dcc1})</td>
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<td>(H_{dcc2})</td>
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<td>0.000</td>
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</table>
Table 10: Average $Q_{20}^a$ component and magnitude of quadrupole $\|Q_{2m}^a\|$ on symmetry equivalent atom sets. See Table 2 for a full description of all the conventions used for labelling symmetry equivalent hydrogen atoms. In $\|Q_{2m}^a\|$, the $m$ denotes that all components $m = 0, 1c, 1s, 2c, 2s$ of the spherical quadrupole tensor are included in the magnitude. All multipoles are spherical, traceless, and in atomic units.

<table>
<thead>
<tr>
<th>Atom</th>
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<th>$|Q_{2m}^a|$</th>
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<td>C_3</td>
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<td>0.029</td>
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<td>0.012</td>
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<td>C_9</td>
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<td>0.026</td>
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<td>0.038</td>
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<td>H_b</td>
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<td>0.035</td>
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<tr>
<td>H_c</td>
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<td>H_cc2</td>
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<tr>
<td>Hdcc1</td>
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</tr>
<tr>
<td>Hdcc2</td>
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<table>
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<tr>
<th>Atom</th>
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<td>1.157</td>
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Table 11: Average $Q_{20}$ component and magnitude of quadrupole $\|Q_{2m}\|$ on symmetry equivalent atom sets ($C_1, C_2, \ldots, H_c$) in PAHs $C_{6n+2}H_{6n}$ $n = 1 - 2$. See Table 2 for a full description of all the conventions used for labelling symmetry equivalent hydrogen atoms and Table 3 for the meaning of $m$ in $\|Q_{2m}\|$. The BS-ISA and GDMA multipoles were partitioned from PBE0(AC) density and the basis used is indicated in the table. All multipoles are spherical, traceless, and in atomic units.

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<th>GDMA aDZ</th>
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<td>Atom</td>
<td>$C_6H_6$</td>
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<tr>
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<th>GDMA aTZ</th>
</tr>
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<tr>
<td>Avg. Moment</td>
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</tr>
<tr>
<td>Atom</td>
<td>$C_6H_6$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.007</td>
</tr>
<tr>
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<td>$H_c$</td>
<td>-0.031</td>
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</table>
Bibliography


[231] Microsoft QDK (pages 130, 133, 155).


