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Going beyond the frozen core approximation: Development of coordinate-dependent pseudopotentials and application to Na_2^+

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Mixed quantum/classical (MQC) simulations treat the majority of a system classically and reserve quantum mechanics only for a few degrees of freedom that actively participate in the chemical process(es) of interest. In MQC calculations, the quantum and classical degrees of freedom are coupled together using pseudopotentials. Although most pseudopotentials are developed empirically, there are methods for deriving pseudopotentials using the results of quantum chemistry calculations, which guarantee that the explicitly-treated valence electron wave functions remain orthogonal to the implicitly-treated core electron orbitals. Whether empirical or analytically derived in nature, to date all such pseudopotentials have been subject to the frozen core approximation (FCA) that ignores how changes in the nuclear coordinates alter the core orbitals, which in turn affects the wave function of the valence electrons. In this paper, we present a way to go beyond the FCA by developing pseudopotentials that respond to these changes. In other words, we show how to derive an analytic expression for a pseudopotential that is an explicit function of nuclear coordinates, thus accounting for the polarization effects experienced by atomic cores in different chemical environments. We then use this formalism to develop a coordinate-dependent pseudopotential for the bonding electron of the sodium dimer cation molecule and we show how the analytic representation of this potential can be used in one-electron MQC simulations that provide the accuracy of a fully quantum mechanical Hartree-Fock (HF) calculation at all internuclear separations. We also show that one-electron MQC simulations of Na_2^+ using our coordinate-dependent pseudopotential provide a significant advantage in accuracy compared to frozen core potentials with no additional computational expense. This is because use of a frozen core potential produces a charge density for the bonding electron of Na_2^+ that is too localized on the molecule, leading to significant overbinding of the valence electron. This means that FCA calculations are subject to inaccuracies of order ∼10% in the calculated bond length and vibrational frequency of the molecule relative to a full HF calculation; these errors are fully corrected by using our coordinate-dependent pseudopotential. Overall, our findings indicate that even for molecules like Na_2^+, which have a simple electronic structure that might be expected to be well-treated within the FCA, the importance of including the effects of the changing core molecular orbitals on the bonding electrons cannot be overlooked. © *2013 American Institute of Physics*.
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I. INTRODUCTION

Computational quantum chemistry presents a major challenge even for modern high-power processors. This is especially true when solving the Schrödinger equation for systems with more than a handful of electronic degrees of freedom, such as most systems in the condensed phase. As such, it is imperative to develop methods that increase the tractability of large quantum calculations without sacrificing quantitative or even qualitative accuracy. One such way of doing so is to employ a mixed quantum classical (MQC) approach, where the majority of the system is treated with classical Newtonian mechanics and a few select, important degrees of freedom are treated quantum mechanically.[1–3] This reduction in the number of electronic degrees of freedom can be accomplished by making a distinction between the *core* and *valence* electrons of a system, where the core electrons are those that remain relatively unaffected by a chemical process of interest and the valence electrons are those that actively participate. In a molecule, for example, the valence electrons are those that actively engage in the bonding between the molecule's constituent atoms, whereas the core electrons are those that are more deeply bound in localized atomic orbitals and/or those that reside on nearby solvent molecules.

To integrate out the core electrons in a MQC calculation, one can take advantage of pseudopotential theory, which allows for the explicit treatment of a system's valence electrons while implicitly including the effects of those electrons that reside in the core.[4] In essence, pseudopotential theory provides an effective potential that replaces the explicit interactions between the core and valence electrons. Although most pseudopotentials are developed empirically and have parameters that are adjusted to reproduce some experimental observable (such as an ionization energy),[4,5] there are formalisms by which pseudopotentials can be rigorously derived.[6,7] Phillips and Kleinman (PK) developed one such formalism that

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allows for the calculation of a pseudopotential using the core orbital wave functions generated from a Hartree-Fock calculation on the system of interest; the formalism finds the potential that guarantees orthogonality between the core and valence wave functions.[4,8] The equations developed by PK, however, are numerically challenging to solve, so this formalism largely has been used only to develop potentials between excess electrons and small closed-shell molecules.[9–14] A few years ago, our group found an alternate derivation of the PK formalism, which provides a numerically and computationally efficient route to the calculation of rigorously derived PK pseudopotentials,[15] even for relatively large and complex molecules.[9,12]

All pseudopotentials, however, whether developed exactly or empirically, are subject to the frozen core approximation (FCA).[16,17] The FCA is a consequence of the fact that a pseudopotential describes the behavior of a set of valence electrons only for a single configuration of the core electrons. If there are situations where the core electrons dynamically change their wave functions, the FCA provides no way to account for this change in the effective interaction with the valence electrons, and some of the undesirable side effects of making the FCA have been discussed in the literature.[18,19] As a gas-phase example of where the FCA can be problematic, consider a diatomic molecule whose bonding electrons are described using pseudopotential theory. At the dissociation limit, the pseudopotential for the valence electrons must be the sum of individual atomic pseudopotentials since there is no interaction between the atoms (hereafter, referred to as a frozen core pseudopotential). As the two atoms approach their equilibrium bond distance, however, a simple sum of atomic pseudopotentials does not correctly describe the bonding. This is because the core orbitals of each atom become distorted from their isolated atomic configurations; the core electrons on one atom are attracted to/polarized by the other atom's nucleus and vice-versa, so the core orbitals start to look less like atomic orbitals and more like molecular orbitals. Thus, a potential that was developed to keep the valence electrons orthogonal to isolated atomic core orbitals is simply not valid for the bound diatomic molecule. This is a breakdown of the frozen core approximation.

In this paper, we show that this type of breakdown can be avoided by calculating the pseudopotential as a function of the internuclear spacing. In effect, we keep track of the changes in the core orbitals by finding the appropriate pseudopotential for any given bond length. As a demonstration that coordinate-dependent pseudopotentials can not only be calculated but also represented in an analytically compact fashion for use in both gas- and condensed-phase molecular simulations, we calculate the full bond-length dependent pseudopotential for the bonding electron of the Na_2^+ molecule, a system that has been given both considerable experimental[20–24] and theoretical consideration.[24–27] We show that with our coordinate-dependent pseudopotential, a one-electron calculation of the electronic structure of Na_2^+ is as accurate as a full Hartree-Fock calculation at all internuclear distances. Moreover, we show that at the equilibrium bond length, one-electron calculations within the FCA predict the wrong shape for the valence electron wave function, overbinding the electron at the center of mass of the Na_2^+ molecule by approximately 0.3 Hartree. This, in turn, leads to FCA errors of roughly 10% in the molecule's bond length, vibrational frequency and valence electron eigenenergy, properties that are all captured accurately when our non-FCA coordinate-dependent pseudopotential is employed. Overall, our results show that it is critical to go beyond the FCA if one wishes to employ MQC techniques to describe chemical systems in which changing nuclear configurations alter the implicitly-treated core orbitals and thus affect the chemical dynamics of interest. And, as we will show in future work, accounting for breakdown of the FCA is particularly important for condensed-phase systems, where fluctuations of nearby solvent molecules can polarize the electrons of a system of interest in a complex, coordinate-dependent fashion.

II. BACKGROUND: MOLECULAR PSEUDOPOTENTIAL THEORY

In this section, we present our method for developing coordinate-dependent pseudopotentials to go beyond the FCA. Our method is based on the PK pseudopotential formalism,[8] so we begin by briefly reviewing the PK method, followed by providing a summary of our reformulation of this method.[15] We then extend this approach to calculate coordinate-dependent pseudopotentials in Sec. III and we illustrate our new process by developing a coordinate-dependent potential that can accurately describe the properties of a gas-phase Na_2^+ molecule over distances ranging from inside the equilibrium bond length to complete dissociation.

A. Philips-Kleinman pseudopotential theory

The PK theory is based on the multi-electron Hartree-Fock (HF) Hamiltonian $\hat{H} = \hat{T} + \hat{U}$, where $\hat{T}$ and $\hat{U}$ are the kinetic and potential energy operators, respectively. The eigenstates of the implicitly-treated n_{core} electrons, which are associated with the occupied orbitals or "core," are given by

$$\hat{H}\,|\psi_i\rangle = \epsilon_i\,|\psi_i\rangle \quad i = 1, \ldots, n_{\text{core}}, \tag{1}$$

while the eigenstate(s) of the explicitly-considered valence electron(s) is (are) given by

$$\hat{H}\,|\psi_v\rangle = \epsilon\,|\psi_v\rangle\,, \tag{2}$$

although in Eq. (2) and what follows we will assume only a single valence electron without loss of generality. A requirement of the HF Hamiltonian is that all of the eigenstates must be orthogonal: $\langle\psi_i|\psi_v\rangle = 0$.[28] The PK formalism builds this orthogonality into the valence wave function without having to explicitly consider the core electrons.[4] This is accomplished by pre-orthogonalizing the wave function of the valence electron to the core orbitals

$$|\psi_v\rangle = |\phi\rangle - \sum_{i=1}^{n_{\text{core}}} |\psi_i\rangle\langle\psi_i|\phi\rangle, \tag{3}$$

where $|\phi\rangle$ is known as the pseudoorbital. By construction, the valence orbital and pseudoorbital have the same eigenenergy[4] and are identical outside the region of the occupied core orbitals, so that the pseudopotential that will be calculated from this pseudoorbital will be norm-conserving.[4,6,7,29] Inserting Eq. (3) for the pre-orthogonalized valence electron wave function back into Eq. (2) yields[8]

$$\hat{H}|\phi\rangle + \sum_{i=1}^{n_{\text{core}}} |\psi_i\rangle\langle\psi_i|(\epsilon - \hat{H})|\phi\rangle \equiv [\hat{H} + \hat{V}_p]|\phi\rangle = \epsilon|\phi\rangle. \tag{4}$$

This expression, known as the Phillips-Kleinman equation, is a one-electron Schrödinger equation for the pseudoorbital in which the pseudopotential $\hat{V}_p$ guarantees that the valence orbital will be orthogonal to the now implicitly-treated core orbitals. This means that the core orbitals need be calculated only once to construct $\hat{V}_p$ and then the properties of the valence electron can be found at the HF level of theory from a one-electron calculation.

The PK equation, however, does not furnish a unique pseudoorbital from which the valence wave function can be obtained via Eq. (3). Cohen and Heine found that extremizing the expectation value of a given operator constrained the system sufficiently to allow for the calculation of a unique pseudoorbital.[30] Upon adding this type of constraint, they showed that the PK pseudopotential equation (Eq. (4)) is transformed into

$$\hat{H}|\phi\rangle + \sum_{i=1}^{n_{\text{core}}} |\psi_i\rangle\langle\psi_i|(\epsilon - \hat{H} + \hat{F} - \bar{F})|\phi\rangle = \epsilon|\phi\rangle, \tag{5}$$

where $\hat{F}$ is the operator whose expectation value $\bar{F} = \langle\phi|\hat{F}|\phi\rangle/\langle\phi|\phi\rangle$ is to be extremized. In most applications,[9,12,15,30] the operator $\hat{F}$ is chosen to be the kinetic energy operator $\hat{T}$ so that the resulting pseudoorbital has the minimum possible kinetic energy and thus is nodeless. Therefore, as long as the core orbitals of a molecule remain fixed (the frozen core approximation), Eq. (5) provides a route to calculating the properties of the valence electron(s) of interest without having to explicitly treat the core electrons.

B. A reformulation of the PK pseudopotential theory

Even with modern computational resources, solving Eq. (5) is still challenging even for modest-sized molecules; examples of the use of this formalism in the literature have typically been restricted to calculating pseudopotentials for excess electrons interacting with small molecules such as water[9,10] or methanol.[11] Previously, however, we showed that when $\hat{F}$ is chosen to be the kinetic energy operator, Eq. (5) is equivalent to[15]

$$|\phi\rangle = \left[\hat{I} - \left(\sum_{i=1}^{n_{\text{core}}} |\psi_i\rangle\langle\psi_i|\hat{T}\right)\Big/\bar{T}\right]^{-1} |\psi_v\rangle \equiv \hat{M}^{-1}|\psi_v\rangle, \tag{6}$$

which replaces the eigenvalue problem with a numerically simple, self-consistent equation for determining $|\phi\rangle$. Equation (6) provides an additional computational advantage in that it does not require evaluation of the potential energy operator and its multi-electron integrals, which is typically the bottleneck in solving equations of this type.

Once $|\phi\rangle$ is calculated from either Eq. (5) or Eq. (6) for a particular system, it is straightforward to calculate the appropriate effective potential U_{eff} (the sum of the pseudopotential and the HF potential energy operator) that is needed in the one-electron Schrödinger equation for the valence electron. We do this by rewriting the effective Hamiltonian in Eq. (4) as $(\hat{H} + \hat{V}_p)|\phi\rangle = (\hat{T} + \hat{U}_{\text{eff}})|\phi\rangle = \epsilon|\phi\rangle$. Then, the nodeless nature of the kinetic-energy minimized $|\phi\rangle$ allows for the otherwise non-local $\hat{U}_{\text{eff}}$ to be localized[15]

$$U_{\text{eff}}^{\text{local}}(\mathbf{r}) = \frac{\langle\mathbf{r}|(\epsilon - \hat{T})|\phi\rangle}{\langle\mathbf{r}|\phi\rangle}. \tag{7}$$

We have used this formalism in previous work to develop potentials for excess electrons interacting with Na^+,[15] water,[9] and tetrahydrofuran.[12]

Overall, our reformulation of the PK theory provides for a computationally efficient determination of a unique, nodeless pseudoorbital (Eq. (6)) and, once $|\phi\rangle$ is determined, rigorously prescribes a local effective, norm-conserving potential (Eq. (7)) that can be used in a one-electron Schrödinger equation that guarantees that the valence electron wave function is orthogonal to the implicitly-included core orbitals. In Sec. III, we build on this formalism as the basis for the principal aim of this work, which is the development of coordinate-dependent pseudopotentials. We note that for the rest of this paper, we use the term *pseudopotential* to describe what is actually the total effective potential given by Eq. (7).

III. COORDINATE-DEPENDENT PSEUDOPOTENTIALS

The formalism presented in Sec. II is computationally efficient, so it is straightforward to apply it not only to molecules of a fixed geometry, as has been done in the past,[9–13] but also to molecules *as a function of geometry*. As we demonstrate in this section, this provides a way to go beyond the FCA by allowing the pseudopotential to incorporate geometry-dependent polarization effects on the core orbitals. As described above, however, the development of PK pseudopotentials is based on the LUMO of the system of interest without the valence electron, rather than the HOMO of the system including the valence electron, so that the relaxation of the core orbitals in the presence of the valence electron is neglected. Since our development of coordinate-dependent pseudopotentials is built on the PK formalism, we also are ignoring this relaxation; instead, the key feature of this work is the development of what is essentially a geometry-dependent frozen core pseudopotential. Because we completely take into account the non-negligible polarization effects of changing nuclear coordinates on the system's core orbitals, our coordinate-dependent pseudopotential allows us to go beyond the fixed geometry that is inherent to the FCA.

To illustrate this, consider the case of using pseudopotential theory to describe the bonding electrons of a diatomic molecule. One can calculate the pseudopotential for this diatomic as a function of the internuclear spacing by keeping track of the changes in the core orbitals and finding the appropriate pseudopotential for any given bond length. The computational efficiency of evaluating Eqs. (6) and (7) makes doing this quite practical. As a demonstration that coordinate-dependent pseudopotentials can not only be calculated but also represented analytically for use in gas- and condensed-phase molecular simulations, in this section we show how to calculate the full bond-length dependent pseudopotential for the Na_2^+ molecule. As discussed further below, *ab initio* calculated energies of the HOMO of Na_2^+ and the LUMO of Na_2^{2+} exhibit negligible quantitative differences, so that the PK formalism should work quite well for this molecule. What we will show next is that accounting for coordinate-dependent polarization effects is important in describing both the electronic and vibrational structure of this deceptively simple molecule.

A. A coordinate-dependent pseudopotential for Na_2^+

To generate a pseudopotential for the interaction between an excess electron and the Na_2^{2+} molecule (as needed to obtain a one-electron description of Na_2^+), the first step is to generate the appropriate kinetic-energy minimized pseudoorbitals. This involves calculating the core electron wave functions of Na_2^{2+} (that is, solving Eq. (1)) at a series of fixed internuclear distances and using these core orbitals in Eq. (6) to generate the set of corresponding pseudoorbitals. Since Na_2^{2+} is a closed-shell molecule, we did this via a restricted Hartree-Fock (RHF) calculation using the GAUSSIAN 03 software package with an atom-centered quadruple-zeta Gaussian-type orbital (GTO) basis set.[31] This is the same basis set we employed in our previous work when constructing a pseudopotential for atomic Na,[15] a level of theory that furnished total and LUMO energies of Na^+ that were within $10^{-5}\%$ and $10^{-3}\%$ of the numerically exact answers, respectively. Once the $\{|\psi_i\rangle\}$ were calculated for Na_2^{2+}, we iteratively solved Eq. (6) using LAPACK routines with a starting guess of the LUMO of Na_2^{2+} ($|\psi_v\rangle$, Eq. (2)). On a 2 GHz Intel Core i7 processor, convergence occurred in less than 1 s of CPU time for each internuclear spacing $\mathbf{R}$.

Once we had the pseudoorbital for each internuclear distance, we then calculated the corresponding localized pseudopotential using Eq. (7). It is important to note that the application of the kinetic energy operator onto the the pseudoorbital in Eq. (7) involves taking the second derivative of $|\phi\rangle$. As we[12,15] and others[10] have discussed previously, the fact that our pseudoorbital is represented in the GTO basis set used in the RHF calculation leads to unphysical asymptotic behavior of this derivative at long range; the e^{-r^2} asymptotic decay of GTOs produces a harmonic binding pseudopotential at long distances. To circumvent this issue, we tapered the pseudopotential we calculated at each internuclear distance to exhibit the correct asymptotic r^{-1} behavior, as described previously.[15]

With the above prescription, we obtained a different set of core orbitals at a variety of internuclear separations, in turn leading to a different pseudopotential for the Na_2^+ molecule at each internuclear distance. To focus on how the pseudopotential changes as a function of this distance (i.e., how the FCA breaks down), we examined how the difference between the calculated molecular pseudopotential and the sum of the atomic pseudopotentials, which is correct in the dissociation limit, varies with internuclear spacing. Thus, for the case of the $Na_2^{2+} - e^-$ interaction, we define the following:

$$(\hat{H} + \hat{V}_p)|\phi\rangle = \epsilon|\phi\rangle, \quad (8)$$

$$\left(\hat{T} + U_{\text{eff}}^{Na_2^{2+}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})\right)|\phi\rangle = \epsilon|\phi\rangle, \quad (9)$$

$$\left(\hat{T} + U_{\text{eff}}^{Na^+}(\mathbf{r}_1) + U_{\text{eff}}^{Na^+}(\mathbf{r}_2) + \xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})\right)|\phi\rangle = \epsilon|\phi\rangle, \quad (10)$$

where $\mathbf{r}_i$ is the distance of the electron from Na nucleus i and $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ is a correction function that takes into account the changes of the core molecular orbitals of Na_2^{2+} as the relative positions of the nuclei change. Defined this way, $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ is a direct measure of the breakdown of the frozen core approximation; it clearly tends toward zero as the internuclear spacing becomes larger than the equilibrium bond length and becomes substantive as the internuclear spacing approaches the equilibrium bond distance. Moreover, the shape of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ shows exactly how the pseudopotential must change in order to guarantee orthogonality of the valence electron(s) to the now-distorted atomic core orbitals as the molecular bond is formed.

By combining Eqs. (9) and (10), we can calculate $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ in a straightforward fashion as

$$\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) = U_{\text{eff}}^{Na_2^{2+}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) - U_{\text{eff}}^{Na^+}(\mathbf{r}_1) - U_{\text{eff}}^{Na^+}(\mathbf{r}_2). \quad (11)$$

Since the last two terms in Eq. (11) are simply the atomic pseudopotentials of the two sodium atoms (which combine to form the fixed-distance frozen core pseudopotential), they are independent of the internuclear spacing and so only need to be calculated once, which we did in Ref. 15. The first term, however, is the pseudopotential for the Na_2^{2+} molecule, which clearly changes as the internuclear distance is varied. We calculated each of these terms (the first one at a variety of internuclear spacings) and then used them to evaluate our correction function $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$. With this correction function and the sum of the atomic pseudopotentials, we now have a rigorously correct pseudopotential at all internuclear spacings for the Na_2^{2+}–e^- interaction that takes into account the formation of (and thus any dynamic changes that might occur in) the core molecular orbitals.

Figure 1 shows two-dimensional cross-sections of $U_{\text{eff}}^{Na_2^{2+}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, $U_{\text{eff}}^{Na^+}(\mathbf{r}_1) + U_{\text{eff}}^{Na^+}(\mathbf{r}_2)$ and $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, where the cross-sections shown are taken through the internuclear bonding axis at $\mathbf{R} = 3.7$ Å, the Hartree-Fock calculated equilibrium bond distance of Na_2^+. Panel (c) of the figure shows clearly that if we were to employ the FCA and describe the molecular bonding using the sum of atomic pseudopotentials, we would overestimate the binding of the electron at the center of mass of the molecule by approximately 0.3 Hartree or an error in the value of the potential at this point of almost 8 eV. The fact that the true attraction of the electron to the space between the nuclei is much less than what would be predicted in the frozen core limit makes physical sense:

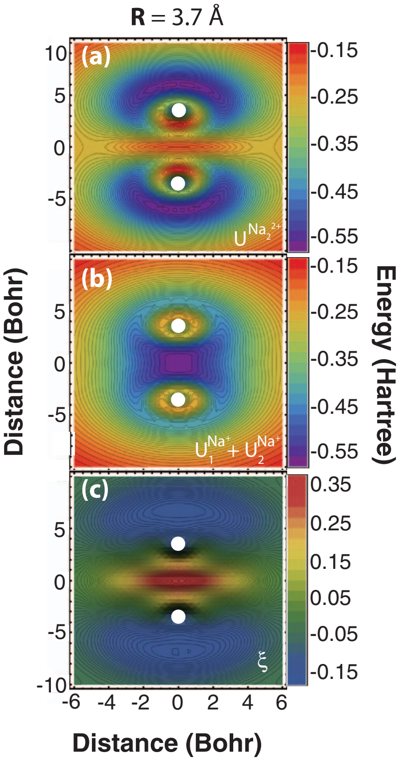

FIG. 1. Cross-sections of (a) $U_{\text{eff}}^{\text{Na}_2^{2+}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, (b) $U_{\text{eff}}^{\text{Na}^+}(\mathbf{r}_1) + U_{\text{eff}}^{\text{Na}^+}(\mathbf{r}_2)$, and (c) $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ (right panel) taken through the bonding axis at an internuclear distance of 3.7 Å. The white dots show the location of the Na^+ nuclei.

the sum of the atomic pseudopotentials does not account for the formation of molecular orbitals, whose electrons would preferentially occupy the region between the two nuclei. This means that the valence (bonding) electron(s) is (are) repelled from this region relative to how they would behave if no core molecular orbitals were formed. This same rationale explains the increased electron attraction in the region near the sodium nuclei, on the outside of the internuclear region: as molecular orbitals form, core electrons are pulled from this area towards the center of the molecule, creating an electron void that is readily occupied by the valence electron(s).

B. Analytic representation of coordinate-dependent pseudopotentials

To determine the full coordinate-dependent pseudopotential for the Na_2^+ molecule, we calculated the **R**-dependence of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ from well inside the equilibrium bond length to the dissociation limit using Eq. (11). The left panels of Fig. 2 show cross-sections of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ calculated for several values of **R**; clearly the magnitude of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ decreases as **R** increases from the equilibrium bond length, as expected for a system that can be adequately described by the sum of atomic pseudopotentials in the dissociation limit.

To analytically describe the behavior of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ as the internuclear separation **R** is varied, we found a single functional form that would capture the important features of ξ and used this function to fit $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ at over a dozen different values for the internuclear distance **R**. The functional form we chose was

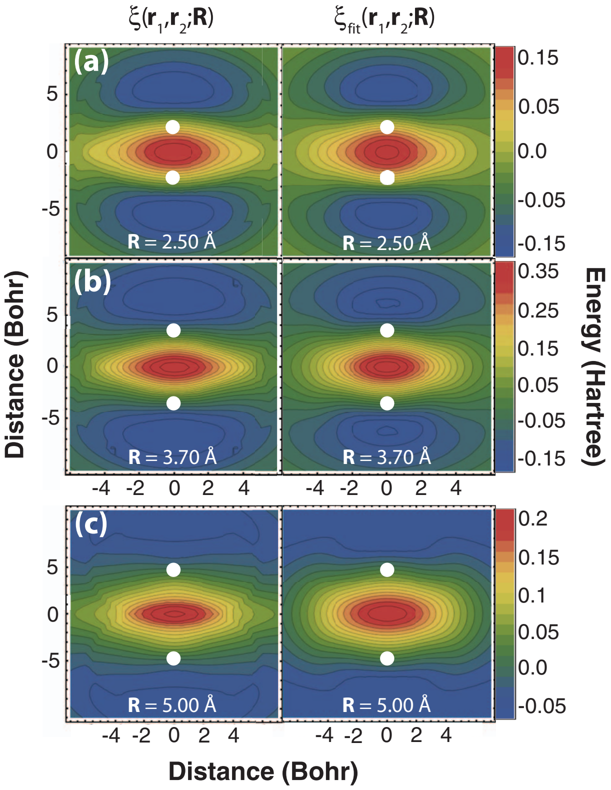

FIG. 2. Slices of the numerically calculated $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ for Na_2^+ (left panels) and fits of these slices (right panels) to Eq. (12). Slices were taken through the bonding axis with internuclear spacings of (a) 2.5 Å, (b) 3.7 Å, and (c) 5.0 Å, and all axis labels are in atomic units. The white dots show the location of the Na^+ nuclei.

$$\xi_{\text{fit}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) = b\left[e^{-c\mathbf{r}_1^2} + e^{-c\mathbf{r}_2^2}\right] + f\left[e^{-g^2\mathbf{r}_1^4} + e^{-g^2\mathbf{r}_2^4}\right] + ie^{-j\mathbf{r}_{\text{com}}^2} + le^{-m\mathbf{r}_{\text{com}}^2}, \tag{12}$$

which consists of two identical atom-centered Gaussian and $e^{-\mathbf{r}^4}$ functions, in addition to two Gaussian functions located at the center of mass (COM) of the sodium dimer cation molecule. This function contains only eight fitting parameters, $b(\mathbf{R})$, $c(\mathbf{R})$, $f(\mathbf{R})$, $g(\mathbf{R})$, $i(\mathbf{R})$, $j(\mathbf{R})$, $l(\mathbf{R})$, and $m(\mathbf{R})$, and we were able to fit $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ with this function with negligible residual contours at all values of **R** using the non-linear least squares fitting routine in *Mathematica 7*. The right panels of Fig. 2 show the fits of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ to Eq. (12) at a few selected internuclear distances; clearly, the functional form we have chosen does an excellent job of representing the corrective term at every internuclear separation.

Now that we have represented the coordinate-dependent pseudopotential at a set of discrete internuclear distances, the next step is to find an analytic way to interpolate the pseudopotential for internuclear separations **R** between the points that we calculated directly and fit to Eq. (12). To do this, we fit the eight fitting parameters used to represent the pseudopotential in Eq. (12) to polynomials of various degrees in **R**. This effectively produces a nested function that provides a continuous analytic expression for how the pseudopotential behaves at any internuclear separation. Figure 3 shows that the fitting parameters behave smoothly as **R** is varied and that the

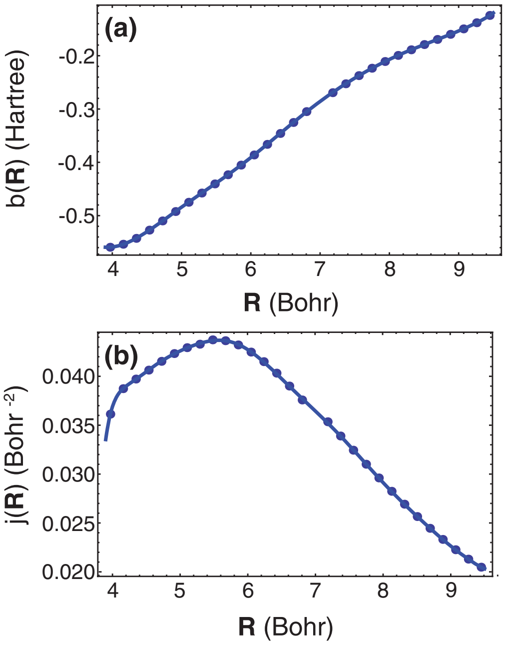

FIG. 3. Bond length (**R**) coordinate dependence (points) of the fitting parameters (a) $b(\mathbf{R})$ and (b) $j(\mathbf{R})$ from Eq. (12), which themselves are fit to (a) twelfth-order and (b) thirteenth-order polynomials, respectively (solid curves), plotted in atomic units.

way the fitting parameters change with internuclear separation can be well captured by a simple polynomial fit. The quality of these fits is equally good for both the linear (e.g., $b(\mathbf{R})$, Fig. 3(a)) and the non-linear (e.g., $j(\mathbf{R})$, Fig. 3(b)) fitting parameters in Eq. (12). Table I summarizes the fitting parameters and polynomial functions used to describe their internuclear distance dependence that completely describes our corrective term $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$. The net result is that one can simply add $\xi_{\mathrm{fit}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ to the sum of the atomic pseudopotentials in a one-electron calculation and obtain the equivalent of a rigorous Hartree-Fock calculation of the exact molecular pseudopotential at any possible internuclear separation. In other words, the fit parameters in Table I contain all of the information of a full distance-dependent Hartree-Fock calculation, boiled down to a single nested function that can be employed in molecular simulation.

In Sec. IV, we apply the analytic coordinate-dependent pseudopotential outlined above to a gas-phase MQC molecular dynamics simulation of the sodium dimer cation. We also compare the results with an identical simulation without the coordinate dependence. In an upcoming paper, we will make this same comparison for the Na_2^+ molecule in solution, and show that the errors associated with making the FCA are even greater, further highlighting the importance of going beyond the frozen core approximation.

IV. DEMONSTRATION OF GOING BEYOND THE FROZEN CORE APPROXIMATION FOR THE SODIUM DIMER CATION

With our newly-developed coordinate-dependent pseudopotential for Na_2^+ in hand (Table I), we are now able to perform mixed quantum classical molecular dynamics simulations of the Na_2^+ molecule. This single-electron MD calculation is fully equivalent to doing *ab initio* molecular dynamics at the HF level. To understand the nature of our formalism and how well it corrects for the breakdown of the FCA, we began this process by calculating the Born-Oppenheimer potential energy surface (PES) for the molecule using our newly-developed coordinate-dependent pseudopotential, and by comparing the results at selected distances to a restricted Hartree-Fock calculation of the LUMO of Na_2^{2+}, upon which our formulation was built.

For our single-electron calculations, we elected to solve the Schrödinger equation in a cubic grid basis, rather than the GTO basis used above. This is because in our upcoming work, we showcase the robustness of our pseudopotential and examine the effects of correcting for the FCA on the dynamics of this molecule in condensed environments, where a grid basis is more appropriate than a traditional quantum chemistry basis.[32,33] Our cubic simulation cell had sides of length 43.8332 Å and included two classical Na^+ nuclei and one fully quantum mechanical electron. The interaction between the two sodium cation nuclei was taken into account via point charge Coulombic repulsion and our coordinate-dependent pseudopotential (Eq. (10) with ξ_{fit} given as in Table I) described the interaction between these classical nuclei and the quantum mechanical electron. The one-electron ground-state wave function for Na_2^+ was calculated every time step (1 fs) on a 24^3 grid with sides of 14 Å centered in the middle of the simulation cell. The forces on the classical Na^+ nuclei from the quantum mechanical electron were evaluated using the Hellmann-Feynman theorem and the nuclear dynamics were propagated using the Verlet algorithm in a manner identical to previous work.[13,33] After employing an initial velocity to the vibrational motion of two classical nuclei, we generated the PES by simply recording the total potential energy (classical + quantum) of the system as the internuclear spacing varied dynamically. Figure 4 displays the dynamically-generated Born-Oppenheimer PES from our one-electron calculations using the coordinate-dependent pseudopotential (orange squares) as well as the LUMO of Na_2^{2+}, generated directly by the RHF calculation (green circles) and the HOMO of Na_2^+, generated via an unrestricted Hartree-Fock (UHF) calculation (black stars); the figure shows that there is excellent agreement between the PES generated from our coordinate-dependent pseudopotential and the LUMO of Na_2^{2+} on which it is based, indicating that our PK formalism and subsequent fitting procedure is robust. Moreover, our single-electron PES not only precisely determines the experimental equilibrium bond length of Na_2^+ (3.7 Å),[21] but also correctly captures both the depth and width of the harmonic well compared to the full RHF calculation. Figure 4 also shows that there are only small energetic differences between the HOMO of the cation and the LUMO of the dication, thus demonstrating that Koopmans' theorem[34] holds nicely for the sodium dimer cation molecule so that the use of the PK formalism is justified.

In addition, the blue hexagons in Figure 4 show an equivalent potential energy surface generated from a one-electron MQC calculation using a frozen core pseudopotential for

TABLE I. Fitting function $\xi_{\rm fit}$ and corresponding parameter functions x (where x represents the general functional form for each of the eight fitting parameters for $\xi_{\rm fit}$) for the coordinate-dependent pseudopotential for the bonding electron of Na_2^+. $\mathbf{R}$ is the internuclear distance in atomic units.

$$\xi_{\rm fit}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) = b[e^{-c\mathbf{r}_1^2} + e^{-c\mathbf{r}_2^2}] + f[e^{-g^2\mathbf{r}_1^4} + e^{-g^2\mathbf{r}_2^4}] + ie^{-j\mathbf{r}_{com}^2} + le^{-m\mathbf{r}_{com}^2}$$

$$x = \sum_{k=0}^{n} x_k \mathbf{R}^k$$

x	n	x_k			
b	12	$b_0 = 6814.2929$	$b_1 = -13767.4654$	$b_2 = 12616.3000$	$b_3 = -6932.0367$
		$b_4 = 2542.9192$	$b_5 = -656.0690$	$b_6 = 122.0744$	$b_7 = -16.5084$
		$b_8 = 1.6107$	$b_9 = -0.1106$	$b_{10} = 5.0760 \times 10^{-3}$	$b_{11} = -1.3983 \times 10^{-4}$
		$b_{12} = 1.7492 \times 10^{-6}$			
c	13	$c_0 = -9473.8160$	$c_1 = 19630.3735$	$c_2 = -18602.2444$	$c_3 = 10674.4553$
		$c_4 = -4138.3551$	$c_5 = 1144.7165$	$c_6 = -232.4476$	$c_7 = 35.0874$
		$c_8 = -3.9376$	$c_9 = 0.3245$	$c_{10} = -0.0191$	$c_{11} = 7.5980 \times 10^{-4}$
		$c_{12} = -1.8327 \times 10^{-5}$	$c_{13} = 2.0243 \times 10^{-7}$		
f	13	$f_0 = -42508.0663$	$f_1 = 88172.7385$	$f_2 = -83628.2563$	$f_3 = 48017.9751$
		$f_4 = -18621.7284$	$f_5 = 5150.7410$	$f_6 = -1045.4650$	$f_7 = 157.6790$
		$f_8 = -17.6733$	$f_9 = 1.4542$	$f_{10} = -8.5388 \times 10^{-2}$	$f_{11} = 3.3892 \times 10^{-3}$
		$f_{12} = -8.1515 \times 10^{-5}$	$f_{13} = 8.9746 \times 10^{-7}$		
g	13	$g_0 = -39537.1850$	$g_1 = 81783.5968$	$g_2 = -77319.7751$	$g_3 = 44239.0469$
		$g_4 = -17091.8621$	$g_5 = 4709.2183$	$g_6 = -952.0817$	$g_7 = 143.0304$
		$g_8 = -15.9694$	$g_9 = 1.3090$	$g_{10} = -7.6587 \times 10^{-2}$	$g_{11} = 3.0294 \times 10^{-3}$
		$g_{12} = -7.2624 \times 10^{-5}$	$g_{13} = 7.9712 \times 10^{-7}$		
i	13	$i_0 = -524718.6533$	$i_1 = 1.0733 \times 10^{6}$	$i_2 = -1.0065 \times 10^{6}$	$i_3 = 572936.8471$
		$i_4 = -220870.9215$	$i_5 = 60896.7238$	$i_6 = -12354.5253$	$i_7 = 1867.4806$
		$i_8 = -210.3373$	$i_9 = 17.4361$	$i_{10} = -1.0341$	$i_{11} = 4.1557 \times 10^{-2}$
		$i_{12} = -1.0143 \times 10^{-3}$	$i_{13} = 1.1359 \times 10^{-5}$		
j	13	$j_0 = -17926.9747$	$j_1 = 37110.7130$	$j_2 = -35169.4293$	$j_3 = 20202.7712$
		$j_4 = -7848.5341$	$j_5 = 2177.5968$	$j_6 = -443.9543$	$j_7 = 67.3448$
		$j_8 = -7.6019$	$j_9 = 0.6307$	$j_{10} = -3.7397 \times 10^{-2}$	$j_{11} = 1.5006 \times 10^{-3}$
		$j_{12} = -3.6533 \times 10^{-5}$	$j_{13} = 4.0762 \times 10^{-7}$		
l	14	$l_0 = 363621.2011$	$l_1 = -701255.3115$	$l_2 = 611226.3598$	$l_3 = -316872.3104$
		$l_4 = 107873.2552$	$l_5 = -24959.9957$	$l_6 = 3859.5651$	$l_7 = -351.0423$
		$l_8 = 4.8911$	$l_9 = 3.5884$	$l_{10} = -0.5660$	$l_{11} = 4.6272 \times 10^{-2}$
		$l_{12} = -2.2732 \times 10^{-3}$	$l_{13} = 6.3772 \times 10^{-5}$	$l_{14} = -7.9100 \times 10^{-7}$	
m	14	$m_0 = -194399.8990$	$m_1 = 392619.3124$	$m_2 = -358117.5278$	$m_3 = 194194.1173$
		$m_4 = -69157.4963$	$m_5 = 16762.9627$	$m_6 = -2729.2175$	$m_7 = 267.0537$
		$m_8 = -6.2871$	$m_9 = -2.4297$	$m_{10} = 0.4204$	$m_{11} = -3.6109 \times 10^{-2}$
		$m_{12} = 1.8447 \times 10^{-3}$	$m_{13} = -5.3563 \times 10^{-5}$	$m_{14} = 6.8568 \times 10^{-7}$	

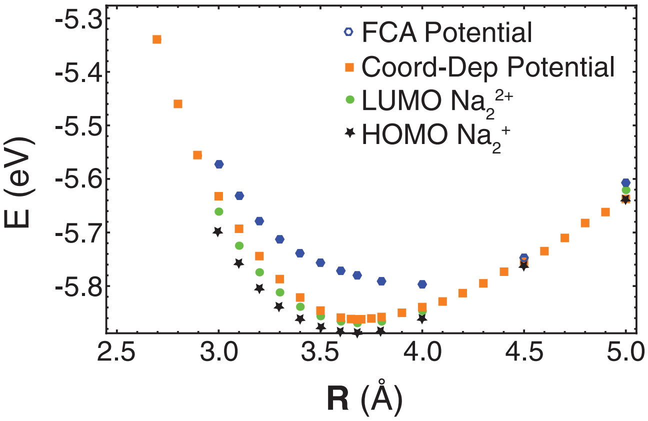

FIG. 4. Gas-phase potential energy surfaces of the Na_2^+ system calculated from MQC MD simulations with a frozen core pseudopotential (blue hexagons), our coordinate-dependent pseudopotential (orange squares) and from fixed-point RHF calculations of the LUMO of Na_2^{2+} (green circles) and UHF calculations of the HOMO of Na_2^+ (black stars) using GAUSSIAN 03.

Na_2^+ (i.e., the sum of the atomic pseudopotentials without the $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ term). The results show that the frozen core picture overestimates the equilibrium bond length by more than 8%. In addition, the bonding well exhibits both a shallower depth and a narrower width than the full RHF result, so that the FCA potential gives a molecular bond that is almost 10% too stiff: the vibrational frequency of the molecule comes in at 113 cm^{-1} and 104 cm^{-1} for the frozen core and coordinate-dependent pseudopotentials, respectively. These errors in the FCA calculation are expected given that the FCA overestimates the attraction of electrons to the center of the molecular bond because the formation of core molecular orbitals is not properly accounted for, as demonstrated above in Fig. 1. Since the only difference between the frozen core potential and our coordinate-dependent pseudopotential is evaluation of the $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ term, this means that the errors associated with the FCA can be avoided in a one-electron calculation with essentially no additional computational

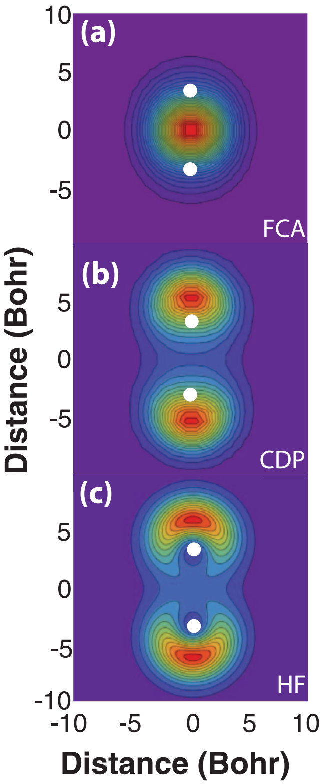

FIG. 5. Charge densities for Na_2^+ calculated from MQC simulations employing (a) a frozen core approximation pseudopotential, (b) our coordinate-dependent pseudopotential (CDP), and (c) one generated from an unrestricted Hartree-Fock calculation using GAUSSIAN 03. The electron density increases from the blue to the red contours, and the purple contour marks zero effective charge density. Calculations were performed at a bond distance of 3.50 Å and slices were taken through the bonding axis. The white dots show the location of the Na^+ nuclei.

expense (beyond that needed to construct the coordinate-dependent potential in the first place).

The magnitude of the bonding error with the FCA approximation is further explored in Figure 5, which compares the calculated electron density from a MQC simulation using the frozen core pseudopotential (panel (a)) to one using our coordinate-dependent pseudopotential (panel (b)) at an internuclear separation of 3.5 Å, slightly inside the equilibrium bond length. The FCA calculation leads to a bonding MO with nearly spherical electron density, whereas the MO computed with the coordinate-dependent pseudopotential shows two distinct lobes of charge density. This is reminiscent of previous theoretical work done on Li_2^+, which also shows two distinct lobes for the valence orbital.[35] Panel (c) in Fig. 5 shows the bonding MO calculated from a UHF calculation using GAUSSIAN 03; clearly, the MQC calculation using our coordinate-dependent pseudopotential does an excellent job of reproducing the full quantum mechanically derived charge density. Thus, the incorrect shape of the MO computed within the FCA leads to an error in the calculated energy of the Na_2^+ system. At an internuclear spacing of 3.7 Å, the total energy (eigenenergy of the valence electron wave function plus the nuclear Coulombic repulsion) from an MQC calculation was found to be −5.78 eV and −5.86 eV using our coordinate-dependent pseudopotential and the frozen core pseudopotential, respectively.

Overall, Figures 4 and 5 clearly indicate that the frozen core approximation cannot properly describe the bonding electron distribution in a molecule, which in turn leads to errors in the calculated bond strength, length, and vibrational frequency. Our newly developed coordinate-dependent pseudopotential, on the other hand, produces not only an accurate qualitative picture of the bonding electron associated with the Na_2^+ molecule, but also allows a single-electron calculation to provide quantitative results that compare well to calculations using a fully quantum mechanical approach at the HF level. In this sense, our coordinate-dependent potential fully accounts for the polarization of the core orbitals, so no additional polarization terms are required to correctly describe the behavior of the valence electrons and thus the bonding of the molecule. We note, however, that the polarization effects accounted for in our potential are only those arising from the presence of the Na–Na bond; many-body polarization effects from external sources are not treated within our formalism. For example, the presence of solvent molecules provides a potential field that can distort the core orbitals in ways not accounted for with our coordinated-dependent pseudopotential. Fortunately, for many applications, solvent molecules affect the valence electrons much more strongly than the core electrons, so that the core electrons could still be implicitly treated with our formalism and a solvent-electron pseudopotential could be used to account for the effects of a condensed environment on the valence electrons. We will show in an upcoming paper that this assumption of pair-wise additivity for coordinate-dependent pseudopotentials internal to the solute of interest and external solvent pseudopotentials works remarkably well for describing molecules like Na_2^+ in solution environments.

V. CONCLUSIONS

We have presented a method for developing coordinate-dependent pseudopotentials and have calculated a coordinate-dependent potential that is valid from bonding to the dissociation limit for the valence electron of the sodium dimer cation molecule. Our method completely takes into account polarization effects on the core molecular orbitals and how these effects change with a change in the nuclear coordinates. Our method is built using a reformulation of the Phillips-Kleinman formalism and is exact in the Hartree-Fock framework, on which the PK method is based. We have shown that for the case of the sodium dimer cation, a molecule for which Koopmans' theorem holds and thus the frozen core approximation might have been expected to work reasonably well, the implementation of a coordinate-dependent pseudopotential that goes beyond the frozen core approximation leads to significant quantitative improvements in calculated molecular properties, including the bond energy, length, and vibrational frequency. Our new method also allows for the calculation of rigorously correct pseudopotentials under conditions where the core molecular orbitals of a system change dynamically during the course of a molecular dynamics simulation. The entire coordinate dependence of the potential can be represented analytically, so that all of the information contained in a coordinate-dependent Hartree-Fock calculation can be reproduced at the single-electron level with a potential that is a single nested function.

In an upcoming paper, we will justify the use of our potential in a more complex environment, as well as show that the coordinate-dependence of the pseudopotential makes an even larger difference for the properties of the sodium dimer cation in the condensed phase, allowing us to gain a much better understanding of the physics involved in the solvent's influence on the electronic structure of a solute's chemical bond.[13] We also expect that going beyond the FCA will make a large impact on other problems, such as the nature of solvated electrons,[9,36–38] for which subtle changes in the functional form of the pseudopotential can cause significant differences in physical interpretation, and we will explore this in future work.

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