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A Computationally-Efficient Exact Pseudopotential Method. I. Analytic Reformulation of the Phillips-Kleinman Theory

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Abstract: Even with modern computers, it is still not possible to solve the Schrödinger equation exactly for systems with more than a handful of electrons. For many systems, the deeply bound core electrons serve merely as place holders and only a few valence electrons participate in the chemical process of interest. Pseudopotential theory takes advantage of this fact to reduce the dimensionality of a multi-electron chemical problem: the Schrödinger equation is solved only for the valence electrons, and the effects of the core electrons are included implicitly via an extra term in the Hamiltonian known as the pseudopotential. Phillips and Kleinman (PK) demonstrated that it is possible to derive a pseudopotential that guarantees that the valence and (implicitly included) core electron wavefunctions are orthogonal. The PK theory, however, is expensive to implement since the pseudopotential is nonlocal and its computation involves iterative evaluation of the full Hamiltonian. In this paper, we present an analytically exact reformulation of the PK pseudopotential theory. Our reformulation has the advantage that the many-electron potential energy operator does not need to be evaluated during the iterative determination of the pseudopotential, greatly increasing the computational efficiency; in the subsequent paper, we show that pseudopotentials for molecules as complex as tetrahydrofuran can be calculated with our formalism in only a few seconds. In addition, our reformulation provides a clear geometric interpretation of how the constraint equations in the PK theory, which are required to obtain a unique solution, are themselves sufficient to calculate the pseudopotential. Finally, our reformulation allows us to extend the theory beyond the frozen core approximation, so that changes in the core wavefunctions due to the presence of the valence electron can be included in the pseudopotential at the level of first-order perturbation theory.

I. INTRODUCTION

In principle, quantum mechanics is not hard; after all, it requires solving only a single well-defined equation: the Schrödinger equation. Yet, for systems where more than a few electrons are involved, even high-power computers cannot manage to solve this equation exactly. Therefore, to make computational progress on many-electron systems, it is imperative to find accurate methods for reducing the number of electronic degrees of freedom. One of the most common reduction methodologies is to differentiate between core electrons and valence electrons. Broadly defined, the core electrons are those low-energy electrons that remain relatively static during most chemical processes and act essentially as place holders; by extension, the valence electrons are those that actively participate in chemical structure and dynamics. The specific way in which the separation between valence and core electrons is determined depends on the system of interest. For atoms and molecules, the valence electrons would be those in the highest energy shell and the remaining electrons would be the core electrons. For solids, the valence electrons would be those that contribute to the valence and conduction bands and the core electrons would be those that remain fixed to the atomic centers. For the scattering of an electron off a closed-shell molecule, the valence electron would be the scattered electron and the core electrons would be all the electrons bound to the molecule.

Given a particular choice of valence and core electrons, our goal is to develop a means to exclude the core electrons from the explicit calculation of the valence-electron wavefunction. However, to accurately calculate the properties of the valence electrons, some implicit information related to the presence of the core electrons must be retained. Regardless of how this is accomplished, the quality of the calculated valence wavefunction depends on how well the implicitly included core electron information approximates the true many-electron potential in the region of interest. One common method for approximating the contribution of the core electrons to the valence electron wavefunction is to use a pseudopotential [1, 2]. There are two major strains of pseudopotential theory [1], model potentials and Phillips-Kleinman-type (PK) potentials. Model potentials, which are most commonly used in DFT calculations [2], are generally not derived from a set of well-defined postulates but are semi-empirically adjusted to reproduce the correct valence electron behavior. In contrast, PK pseudopotentials, which are used in a variety of fields and particularly for the potentials in mixed quantum/classical molecular dynamics simulations (e.g. [3–6]), are based on a rigorously derivable quantum mechanical formalism.

For large systems, calculation of the PK pseudopotential is expensive or requires making approximations, which is why the model approach is often more desirable. The challenge of building accurate model potentials, in turn, is that they require good intuition for the electronic wavefunctions. For atoms, the core wavefunctions are relatively simple and well understood; thus, very accurate models can be created, and many of these have found utility in solid-state calculations [2]. For molecules, however, the same level of intuitive knowledge is usually not available due to the complexity and variety of molecular wavefunctions. Since the model approach becomes increasingly less reliable for more complex systems, there is clearly a need to extend the analytically rigorous PK pseudopotential theory to systems that it currently cannot handle.

In this paper, we introduce an analytically exact reformulation of the standard PK pseudopotential theory that not only provides a large improvement in computational effort but also is more physically transparent. As we will show below, our formulation allows the calculation of exact PK pseudopotentials without the need to evaluate the computationally expensive potential energy operator. The rest of this paper is organized as follows: First, a brief discussion of PK pseudopotential theory will be given in Section II A. In Section II B, we will present our new computationally efficient pseudopotential formalism, and provide a physical interpretation of how the new equations furnish a rigorous effective potential. In Section III, we will discuss some of the implications of our new formalism, and speculate on some possible additional uses, including extension of the formalism beyond the frozen core approximation. We finish with a few concluding remarks in Section IV.

II. A REFORMULATION OF PK PSEUDOPOTENTIAL THEORY

To place our work in context, in Section II A we first present a derivation of the PK pseudopotential formalism, which can be applied to any system where the core/valence electron separation is a good approximation. We will focus our discussion on the development of the pseudopotential for the case of only one valence electron, but the formalism can be extended to treat multiple valence electrons in a straightforward manner (see, e.g., Ref. [1] and references therein). We then develop our new extension of the PK method in Section II B and discuss the computational advantages and physical insight gained through our reformulation in Section II C.

A. Basic PK Pseudopotential Theory

For a given multi-electron Hamiltonian (e.g. the Hartree-Fock Hamiltonian), $\hat{H} = \hat{T} + \hat{U}$, where $\hat{T}$ is the kinetic energy operator and $\hat{U}$ is the potential energy operator, the core electron wavefunctions (of which there are *ncore*) are defined by the Schrödinger equation,

$$\hat{H}|\psi_i\rangle = \epsilon_i|\psi_i\rangle \qquad (i = 1, ncore). \tag{1}$$

The valence electron wavefunction for this same Hamiltonian is given by,

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

Of course, the valence electron wavefunction is orthogonal to all of the core electron wavefunctions ($\langle\psi_v|\psi_i\rangle = 0$ for all i), and this orthogonality must always be preserved, even if the core electrons are no longer treated explicitly. One way to guarantee this orthogonality is to write the valence electron wavefunction in a basis set that is *a priori* orthogonalized to the core electrons. This *pre-orthogonalization* is the foundation of pseudopotential theory. Using this idea, we can orthogonalize any arbitrary basis set $\{|f_n\rangle\}$ to the core electron wavefunctions by defining,

$$|\chi_n\rangle = |f_n\rangle - \sum_{i=1}^{ncore} \langle\psi_i|f_n\rangle|\psi_i\rangle, \tag{3}$$

where each member of the this new basis set, $\{|\chi_n\rangle\}$, satisfies $\langle\chi_n|\psi_i\rangle = 0$ for each $|\psi_i\rangle$. The valence electron wavefunction can then be expressed as a linear combination of the states in this new basis set,

$$|\psi_v\rangle = \sum_n c_n|\chi_n\rangle. \tag{4}$$

Using the definition of the pre-orthogonalized $\{|\chi_n\rangle\}$ above, we can re-express Eqn. 4 as,

$$|\psi_v\rangle = |\phi\rangle - \sum_{i=1}^{ncore} |\psi_i\rangle\langle\psi_i|\phi\rangle \equiv |\phi\rangle - \hat{\Omega}|\phi\rangle \tag{5}$$

where we have introduced the projection operator onto the set of core electrons wavefunctions, $\hat{\Omega}$,

$$\hat{\Omega} = \sum_{i=1}^{ncore} |\psi_i\rangle\langle\psi_i|\,, \tag{6}$$

and a new function that results from a linear combination of the $|f_n\rangle$, designated the pseudo-orbital,

$$|\phi\rangle = \sum_n c_n |f_n\rangle. \tag{7}$$

This approach of describing the valence electron wavefunction in a pre-orthogonalized basis set has been studied and used extensively as a computational tool [7]. It took the insight of Phillips and Kleinman [8], however, to note that the geometrical constraint of pre-orthogonalization to the core wavefunctions could be expressed as an additional repulsive potential, called the pseudopotential, and that the psuedo-orbital, $|\phi\rangle$, has an important physical interpretation. To derive an equation for the pseudopotential, we can substitute Eqn. 5 into Eqn. 2, resulting in a *one-electron* equation for $|\phi\rangle$,

$$\hat{H}|\phi\rangle + \sum_{i=1}^{ncore} (\epsilon - \epsilon_i)\langle\psi_i|\phi\rangle|\psi_i\rangle = \epsilon|\phi\rangle. \tag{8}$$

This equation has the form of our original valence eigenequation (Eqn. 2), but with an extra term arising from the pre-orthogonalization. This extra term, the pseudopotential, $\hat{V}_p \equiv \sum_{i=1}^{ncore}(\epsilon - \epsilon_i)|\psi_i\rangle\langle\psi_i|$, is a non-local operator, and the pseudo-orbital, $|\phi\rangle$, is an eigenstate of the new effective Hamiltonian, $\hat{H} + \hat{V}_p$. In this paper, we refer to the pseudopotenial strictly as the additional term $\hat{V}_p$, and we use the term 'effective Hamiltonian' to refer to the original Hamiltonian plus the pseudopotential. Eqn. 8 shows that the pseudo-orbital has the same eigenenergy, ϵ, as the valence electron; moreover, as can be shown by a straightforward variational argument, the pseudo-orbital is the ground-state solution of the effective Hamiltonian. Thus, even though the pseudopotential operator is non-local, the fact that $|\phi\rangle$ is nodeless allows $\hat{V}_p$ to be easily localized (i.e. allows the construction of a potential that is completely defined by a single spatial coordinate),

$$V_p^{local}(\mathbf{r}) = \frac{\langle\mathbf{r}|\hat{V}_p|\phi\rangle}{\langle\mathbf{r}|\phi\rangle}. \tag{9}$$

Thus, the PK pseudopotential formalism provides a method to solve the reduced electron problem by adding a *local* potential to the original Hamiltonian to guarantee that the valence electron wavefunction is orthogonal to the core electron wavefunctions. As can be seen in Eqn. 5, $|\phi\rangle \rightarrow |\psi_v\rangle$ in regions where $|\phi\rangle$ does not overlap with the $|\psi_i\rangle$'s, that is, outside the core. Therefore, the pseudopotential formulation allows for an accurate calculation of the valence electron wavefunction as long as the specific details of the valence electron wavefunction inside the core region are not important, as is true for most chemical and materials applications. For cases where more detail is required, the information about the valence wavefunction in the core region can be backed out of $|\phi\rangle$ using Eqn. 5.

Despite all the advantages of this theory, there still exists a fundamental ambiguity; the solution $|\phi\rangle$ of Eqn. 8 is not unique [9]. This is because for any solution $|\phi\rangle$, the function $|\phi^{'}\rangle$, defined by,

$$|\phi^{'}\rangle = |\phi\rangle + \sum_{i=1}^{ncore} a_i|\psi_i\rangle \equiv |\phi\rangle + |\delta\phi\rangle \tag{10}$$

is also a solution of Eqn. 8 for arbitrary a_i. To remove this ambiguity, we can apply an additional constraint without affecting the physics of the problem. If we choose our constraint to extremize the expectation value $\bar{F}$ of an arbitrary observable $\hat{F}$, given by

$$\bar{F} = \frac{\langle\phi|\hat{F}|\phi\rangle}{\langle\phi|\phi\rangle}, \tag{11}$$

then setting the first variation [10] of this expectation value, $\delta\bar{F}$, equal to zero gives,

$$\langle\delta\phi|\phi\rangle\bar{F} = \langle\delta\phi|\hat{F}|\phi\rangle. \tag{12}$$

Substituting the allowed variation of the pseudo-orbital (Eqn. 10) into Eqn. 12 leads to the following constraint equations,

$$\langle\psi_i|\hat{F} - \bar{F}|\phi\rangle = 0 \qquad i = 1, \cdots, ncore. \tag{13}$$

The modification of PK pseudopotential theory to incorporate the generalized constraint is now straightforward. First, we recast the constraint Eqns. 13 by multiplying each equation by its corresponding core-electron wavefunction and summing to give,

$$\sum_{i=1}^{ncore} |\psi_i\rangle\langle\psi_i|\hat{F} - \bar{F}|\phi\rangle = 0. \tag{14}$$

Now, using Eqn. 2, Eqn. 8 can be rewritten as,

$$\hat{H}|\phi\rangle + \sum_{i=1}^{ncore} |\psi_i\rangle\langle\psi_i|\epsilon - \hat{H}|\phi\rangle = \epsilon|\phi\rangle. \tag{15}$$

Adding zero in the form of Eqn. 14 to Eqn. 15 results in the fundamental equation for the pseudo-orbital with a generalized constraint,

$$\hat{H}|\phi\rangle + \sum_{i=1}^{ncore} |\psi_i\rangle\langle\psi_i|\epsilon - \hat{H} + (\hat{F} - \bar{F})|\phi\rangle = \epsilon|\phi\rangle. \tag{16}$$

Clearly, a solution to Eqn. 16 also will be a solution to Eqns. 8 and 14. Using the projection operator defined in Eqn. 6, the (non-local) pseudopotential operator with a generalized constraint is,

$$\hat{V}_p = \hat{\Omega}[\epsilon - \hat{H} + (\hat{F} - \bar{F})]. \tag{17}$$

As an example, one common constraint is to minimize the kinetic energy of the psuedo-orbital ($\hat{F} = \hat{T}$), and in this case the pseudopotential operator becomes $\hat{V}_p = \hat{\Omega}[\epsilon - \hat{U} - \bar{T}]$ since $\hat{H} = \hat{T} + \hat{U}$.

Although this formalism can be used to find an approximate reduced-dimensionlity solution for the valence electron wavefunction that remains orthogonal to the (now implicitly included) core electrons, it is not precisely clear how to think physically about the pseudopotential. Perhaps the most insightful and intuitive example of pre-orthogonalization is illustrated by the calculation of the properties of the conduction electrons in solids. In the first half of the last century, such calculations were hindered by the large number of plane wave basis states required for an accurate solution. Typically, the valence electron wavefunctions outside the region of the atomic cores are smoothly varying; however, many additional high-frequency basis states are necessary to account for the rapid oscillation of the valence electrons in the region of the atomic centers that arises from the enforcement of orthogonality between the core and valence electrons. Herring suggested that the number of plane wave basis states could be dramatically reduced by pre-orthogonalizing the plane waves to the atomic core wavefunctions [7]. In his orthogonalized plane-wave (OPW) formalism, the basis states are given by,

$$|OPW; k\rangle = e^{i\vec{k}\cdot\vec{r}} - \sum_i \langle\psi_i|e^{i\vec{k}\cdot\vec{r}}\rangle\psi_i(\vec{r}). \tag{18}$$

By pre-orthogonalizing, the valence electron wavefunction can be accurately expressed with low-frequency OPWs, even in the region of the core. Later analysis [1] showed that the effective potential energy of the valence electron in the core region is largely constant because the large kinetic energy of the valence electron resulting from the high-frequency oscillations required to orthogonalize it to the core wavefunctions is essentially cancelled by the attractive nuclear Coloumb potential. Thus, the use of a smooth valence wavefunction in the region of the core can be intuitively justified if the pre-orthogonalization is equivalent to adding an additional repulsive potential to balance the nuclear attraction; Phillips and Kleinman proved this equivalence [8]. This cancellation holds not just for the case of a plane wave basis (after all, Eqn. 18 is just a special case of Eqn. 3) but is independent of the choice of basis set. Indeed, this cancellation is a hallmark of the pseudopotential method, as demonstrated explicitly by Cohen and Heine [9].

B. A New Computationally-Efficient Pseudopotential Formalism

Although the formalism of the previous section is on firm ground, there are two practical issues that have limited the use of exact PK pseudopotentials. First, the core eigensolutions to the Hamiltonian, $\hat{H}$, must be found. Since this can be computationally expensive, several approximations have been introduced. For example, instead of explicitly solving for the core electron wavefunctions, model pseudopotential methods have been developed by Heine and Abarenkov [11] and Shaw [14] that rely on analytic approximations to these wavefunctions. As mentioned in the Introduction, these wavefunction estimates are often very good for atoms, but become increasingly unreliable for higher-complexity systems such as molecules. Another approach has been to solve for the core eigenvectors using a simplified Hamiltonian; for example, the exchange potential can be neglected [12]. Although these approximate methods often produce accurate physical results, this is not always the case. For instance, we have found that a straightforward application of the Heine-Abarenkov [11] method to treat the two valence electrons of the sodium anion produced highly unphysical results, but that the sodium anion valence electrons were correctly described using the exact PK formalism [13]. Fortunately, modern computational power has largely dated any concerns about obtaining full solutions to the core electron wavefunctions, at least for atoms and small molecules.

Even with accurate solutions for the core wavefunctions, however, we still face a second practical issue when solving Eqn. 16: This equation must be solved self-consistently, which is computationally expensive due to the need for repeated evaluation of the two-electron integrals in the multi-electron Hamiltonian. In fact, the solution to Eqn. 16 can be so cumbersome that the only published applications of which we are aware are for atoms and small molecules, such as water [15, 16]. In this section, we will show that there is an analytically exact reformulation of the generalized PK pseudopotential theory that is much more computationally efficient to solve and, at least for us, more physically transparent. The advantage of our pseudopotential formulation is that the pseudo-orbital can be calculated without the need to iteratively evaluate any two-electron integrals: With the appropriate choice of $\hat{F}$, our formalism avoids the evaluation of the potential energy operator entirely.

We begin by re-examining Eqn. 16, the expression that allows for a unique determination of the pseudo-orbital in the presence of a constraint,

$$\left[\hat{H} + \hat{\Omega}\left(\epsilon - \hat{H} + \hat{F} - \bar{F}\right)\right]|\phi\rangle = \epsilon|\phi\rangle. \tag{19}$$

where the core-orbital projection operator $\hat{\Omega}$ is defined in Eqn. 6. If we choose minimization of the kinetic energy of the pseudo-orbital as our constraint (i.e. $\hat{F} = \hat{T}$) and note that $\hat{H} = \hat{T} + \hat{U}$, then Eqn. 19 becomes,

$$\left[\hat{H} + \hat{\Omega}(\epsilon - \bar{T} - \hat{U})\right]|\phi\rangle = \epsilon|\phi\rangle \tag{20}$$

where $\bar{T} = \langle\phi|\hat{T}|\phi\rangle$. Making use of the fact that for most situations, $\left[\hat{\Omega}, \hat{H}\right] = 0$, which implies that $\hat{\Omega}\hat{U} = \hat{T}\hat{\Omega} - \hat{\Omega}\hat{T} + \hat{U}\hat{\Omega} = \hat{H}\hat{\Omega} - \hat{\Omega}\hat{T}$, Eqn. 20 can be rewritten as,

$$(\hat{H} - \epsilon)(|\phi\rangle - \hat{\Omega}|\phi\rangle) - \bar{T}\hat{\Omega}|\phi\rangle + \hat{\Omega}\hat{T}|\phi\rangle = 0. \tag{21}$$

We can now substitute Eqn. 5 into Eqn. 21 and make use of Eqn. 2 to obtain,

$$|\phi\rangle = |\psi_v\rangle + \sum_{i=1}^{ncore} \frac{\langle\psi_i|\hat{T}|\phi\rangle}{\bar{T}}|\psi_i\rangle. \tag{22}$$

Equation 22 can now serve as the operational definition of the pseudo-orbital $|\phi\rangle$ when $\hat{T}$ is extremized: in other words, Eqn. 22 is equivalent to Eqn. 16 for the choice $\hat{F} = \hat{T}$ as long as $\left[\hat{\Omega}, \hat{H}\right] = 0$. In the following section we will generalize Eqn. 22 to include cases where the commutation does not hold, but for most cases of interest, Eqn. 22, is sufficient to determine the pseudo-orbital and thus the pseudopotential. The recognition that Eqn. 22 is analytically equivalent to Eqn. 16 is the principle result of this work.

Although the derivation of Eqn. 22 is simple, it provides a powerful tool in that it is the most computationally-efficient exact PK pseudopotential equation. Critical to the efficiency is the fact that we made the standard choice to minimize the kinetic energy of the pseudo-orbital: Even though the pseudo-orbital must still be evaluated self-consistently, Eqn. 22 avoids any explicit calculation of the potential energy operator with its multi-electron integrals. This sidesteps the major computational bottleneck in computing exact PK pseudopotentials, and, due to the iterative nature of solving the equation, the computational savings will be multiplied. Once the pseudo-orbital has been calculated by solving

Eqn. 22, it is straightforward to calculate the pseudopotential, $V_p(\mathbf{r})$. For most applications, however, only the total effective potential, $\hat{U}_{eff} = \hat{U} + \hat{V}_p$, is needed. Since $\hat{H} = \hat{T} + \hat{U}$ and the pseudo-orbital is nodeless, we can easily obtain the localized effective potential, U^{local}_{eff}, by,

$$U^{local}_{eff}(\mathbf{r}) = \frac{\langle \mathbf{r} | \left(\epsilon - \hat{T} \right) | \phi \rangle}{\langle \mathbf{r} | \phi \rangle}. \tag{23}$$

Thus, by choosing kinetic energy minimization in the context of Eqn. 22, we not only have avoided the iterative calculation of the troublesome two-electron terms to determine the pseudo-orbital, but we also can find the local effective potential without ever having to explicitly calculate the potential energy. Of course, information about the potential energy is implicitly included along with the core electron wavefunctions, but once the core electron solutions are found, the construction of the effective potential does not require any additional potential energy evaluations. Because kinetic energy minimization allows for the complete exclusion of the potential energy operator, it difficult to imagine that any other choice of $\hat{F}$ could provide a more efficient route to calculating $U^{local}_{eff}(\mathbf{r})$; thus, Eqns. 22 and 23 provide a new operational method for calculating the exact pseudo-orbital and effective potential.

In the following paper [17], we discuss several important implementation issues of this formalism for the calculation of pseudopotentials for large, complex molecules. In particular, we apply our formalism to calculate the effective potential between an excess electron and tetrahydrofuran (THF) molecule, which, as far as we are aware, is now the most complicated molecule for which an exact pseudopotential has been determined. One particularly critical issue is that the stability of the numerical solution of Eqn. 22 is sensitive to the choice of computational methodology; see reference [17]. However, with an appropriate implementation, the numerical solution of Eqn. 22 is computationally trivial: once the core wavefunctions were determined, calculation of the excess electron-THF effective potential via Eqns. 22 and 23 took less than 10 s on a single 1.3 GHz Athlon AMD processor.

C. Discussion: A Geometric Interpretation of Pseudopotential Theory

Eqn. 5 shows that, in some sense, the critical piece of information required to form the pseudo-orbital is understanding how it overlaps with the core electron wavefunctions. Unfortunately, there are an infinite number of ways this overlap can occur, as can be seen from Eqn. 10. This is why it is impossible to construct the pseudopotential in the unconstrained

PK formalism: Eqn. 8 has no unique solution. As mentioned above, a unique solution can be found by introducing an arbitrary constraint, which results in additional terms in the pseudopotential operator, $\hat{V}_p$. The resulting eigenequation, Eqn. 16, can then be used to find a unique solution for the pseudo-orbital. However, our formalism provides a new unique method to write the overlap term of Eqn. 5, which allows us to replace Eqn. 16 by Eqn. 22. In fact, a comparison of Eqn. 22 with Eqn. 5 provides a unique expression for the pseudo-orbital/core electron wavefunction overlap with the minimum kinetic energy constraint,

$$\langle\psi_i|\phi\rangle = \frac{\langle\psi_i|\hat{T}|\phi\rangle}{\bar{T}}. \tag{24}$$

Although Eqn. 22 provides a new means to solve for the unique, constrained pseudo-orbital, further examination of the ambiguity in the unconstrained $|\phi\rangle$ is fruitful. The ambiguity arises because the act of pre-orthogonalization (which is equivalent to writing the pseudopotential) creates a linearly-dependent basis set [9]. The basis set for the original all-electron problem, $\{|f_n\rangle\}$, is linearly-independent by construction, and pre-orthogonalization of this basis (Eqn. 3) creates a one-to-one transformation of the $\{|f_n\rangle\}$ to the respective $\{|\chi_n\rangle\}$. This process, however, involves subtracting off the overlap of the $\{|f_n\rangle\}$ with the core wavefunctions, but the core wavefunctions also depend on the $\{|f_n\rangle\}$. Thus, the pre-orthogonalization transformation from the $\{|f_n\rangle\}$ to the $\{|\chi_n\rangle\}$ destroys the linear-independence of the basis set. A geometric interpretation is that pseudopotential theory acts to precisely reduce the dimensionality of the all-electron Hilbert space. By pre-orthogonalizing the original basis set (Eqn. 3) and writing the valence electron wavefunction in the set of pre-orthogonalized vectors, we are by definition excluding the valence electron wavefunction from occupying any part of the Hilbert space spanned by the core electron eigenfunctions. In other words, we are restricting the valence electron wavefunction to a surface in Hilbert space that has $ncore$-lower dimensionality than the full multi-electron wavefunction. However, due to the one-to-one nature of the basis transformation, we are using the same size basis set to describe this lower-dimensional space; therefore, the $\{|\chi_n\rangle\}$ must be linearly-dependent [18]. This linear dependence is why the pseudo-orbital cannot be uniquely determined without additional constraints.

In order to uniquely describe the pseudo-orbital, a linearly-independent set of basis states that spans the lower-dimensional space is required; this new basis is made to be linearly independent by adding the set of *ncore* constraint equations (Eqn. 13) to the original basis states. Moreover, these constraints are surprisingly fundamental: with some simple algebra, it can be shown that Eqn. 22 is equivalent to Eqn. 14, indicating that the constraint equations themselves contain all of the essential physics underlying PK pseudopotential theory. It is worth noting that the form of the constraint equations is restricted to only those variations (Eqn. 10) that are also solutions to the original PK equation (Eqn. 8). In other words, Eqn. 22 tell us that we can choose *any* pseudo-orbital so long as the pre-orthogonalization to the core wavefunctions is preserved: as long as the pseudo-orbital is constrained to the correct surface in Hilbert space, the choice of the reduced-dimensionality basis set is arbitrary. Since the surface geometry is completely defined by the core electron wavefunctions, it implicitly includes all of the information about the core electrons, so the constraint equations uniquely define how to reduce the dimensionality for the extremization of any particular operator. Thus, as long as the core electronic wavefunctions are known, they can be projected out exactly. But what if this is not the case? The analysis of this question leads to a generalization our formalism that is presented in the next section.

III. GENERALIZATION OF THE PK PSEUDOPOTENTIAL FORMALISM

In this section, we generalize our new pseudopotential formalism to include cases where the implicit assumptions in the theory break down. The most basic assumption in pseudopotential theory is that the core electrons can be accurately represented by one-electron spinorbitals, i.e. the theory is restricted to Hartree-Fock-type Hamiltonians. This is, from a practical point of view, absolutely necessary and is a feature of virtually all electronic structure theory. However, even if the correlation between core electrons makes the orbital separation impossible, a pseudopotential formalism can be written for an unseparable multi-electron core wavefunction [19], but this formalism is impractical to implement and has found utility primarily as a formal foundation for the development of model pseudopotentials [1]. The main assumption in our particular development of the theory is that $\left[\hat{\Omega}, \hat{H}\right]$ $= 0$, so that the constraints can be separated to uniquely determine the pseudo-orbital. In this section, we generalize our formalism to include the case where this assumption breaks down.

What can cause the breakdown of $\left[\hat{\Omega}, \hat{H}\right] = 0$? We will (somewhat arbitrarily) separate the breakdown of this commutation into two classes: failure due to methodology, and failure due to unincorporated physics. One example in the class of methodological failures for which the commutation breaks down is the use of a Hamiltonian that does not treat the core and valence electrons identically [1]. To overcome this, Weeks and Rice have derived a general matrix equation for projecting arbitrary core functions onto an arbitrary set of functions to give a unique solution to the pseudopotential equation [20]. To the best of our knowledge, however, no recent work has attempted to use this matrix formalism, instead researchers have chosen Hamiltonians whose pseudopotentials can be calculated by solving Eqn. 16.

In addition to methodological failures, our formalism can fail due to unincorporated physics. Throughout this paper we have been implicitly assuming that the core electronic wavefunctions are static; in other words, that the core electron wavefunctions are not altered by the presence of the valence electron. This frozen-core approximation is in general not valid: it requires, for example, that the core electron wavefunctions be the same for an isolated atom in the gas phase as for the same atom in a solid or liquid. Our interest in removing the frozen-core approximation comes in the context of mixed quantum/classical molecular dynamics simulation, of which a prototypical example is the simulation of the hydrated electron [21–23]. In such simulations, the 'valence' solvated electron wave function is treated explicitly and its interaction with the 'core' electrons in the closed-shell water molecules are treated via a pseudopotential. Because such e^--H_2O pseudopotentials [12, 15] are calculated using the core wavefunctions of an isolated gas-phase water molecule, the simulations implicitly assume that the effective potential between the excess electron and each water molecule in the condensed phase is the same as that in the gas phase. Of course, the electric fields from both the solvated electron and the other water molecules will polarize the core electrons on the water molecules and alter their wavefunctions from that in the gas-phase. This polarization effect needs to be small (in the perturbative sense) or else the simulation of such systems would fall outside the regime where pseudopotential theory is applicable. If there are changes in the core electron wavefunctions upon introduction into the condensed-phase environment, then the multi-electron quantum problem cannot be reduced to as great an extent: the core/valence separation becomes invalid because the core electrons do in fact participate in the physical process. (Note that assuming that the changes in the core electron wavefunctions must be small is not the same as assuming that the overall effect of polarization on the dynamics of the system is small.)

To account for this polarization effect of the core electrons in mixed quantum/classical simulations an extra term is often added to the effective Hamiltonian [1, 12]. The addition of such a term can be accurate for atoms and very small, approximately spherical molecules such as water because it is straightforward to write a meaningful site-based polarization approximation. For larger non-spherical molecules, however, this procedure becomes increasingly dubious because the molecular core-electron wavefunctions, particularly the higher-energy core electrons that are the most likely to be significantly polarized, will typically not be centered on a single atomic site.

What we will show next is that polarization effects can be included in our pseudopotential formalism at the level of first-order perturbation theory. To include polarizability into our theory, the principal piece of information required is how the core orbitals are altered in the presence of a perturbing field. For a perturbing field described by $\hat{H}_I$, the full Hamiltonian is $\hat{H} = \hat{H}_o + \hat{H}_I$, where $\hat{H}_o$ is the original, unperturbed Hamiltonian. Given the core orbitals of the original Hamiltonian, $\{|\psi_i^o\rangle\}$, the corrections to the core wavefunctions in the presence of the perturbation are approximated in first-order perturbation theory by,

$$|\psi_i^I\rangle = \sum_{j\neq i}^{ntot} \frac{\langle\psi_j^o|H_I|\psi_i^o\rangle}{\Delta\epsilon_{ji}}|\psi_j^o\rangle, \tag{25}$$

where *ntot* is the total number of eigenstates of H_o and $\Delta\epsilon_{ji} = \epsilon_j - \epsilon_i$. We can now define the core-electron projection operator for the perturbed core wavefunctions, $\hat{\Omega} = \hat{\Omega}_0 + \hat{\Omega}_I$, where the unperturbed projection operator $\hat{\Omega}_0$ is given by Eqn. 6 and projection operator for the perturbation correction is,

$$\hat{\Omega}_I = |\psi_i^0\rangle \sum_{j\neq i}^{ntot} \frac{\langle\psi_i^0|\hat{H}_I|\psi_j^0\rangle}{\Delta\epsilon_{ji}}\langle\psi_j^0| + \sum_{j\neq i}^{ntot} \frac{\langle\psi_j^0|\hat{H}_I|\psi_i^0\rangle}{\Delta\epsilon_{ji}}|\psi_j^0\rangle\langle\psi_i^0| \tag{26}$$

where we have neglected terms of $\mathcal{O}(\hat{H}_I)^2$.

When $\left[\hat{\Omega}, \hat{H}\right] \neq 0$, it is straightforward to show that Eqn. 22 becomes

$$(1 + \frac{[\hat{\Omega}, \hat{H}]}{\bar{T}})|\phi\rangle = |\psi_v\rangle + \sum_i \frac{\langle\psi_i|\hat{T}|\phi\rangle}{\bar{T}}|\psi_i\rangle. \tag{27}$$

for the case of the PK pseudopotential with the minimum kinetic energy constraint. Now that all the required pieces are in place, we can find an equation for the pseudo-orbital in the presence of a perturbing field. With some simple algebra, Eqn. 27 reduces to

$$\hat{\Omega}_I(\hat{T} - \bar{T})|\phi\rangle = [\hat{\Omega}_I, \hat{H}_I]|\phi\rangle. \tag{28}$$

as the operative equation that determines the pseudo-orbital when the core orbitals are perturbed. Note that even in this perturbative scheme, there is no need to evaluate any two-electron integrals since $[\hat{\Omega}_I, H_o] = 0$.

We are currently in the process of exploring the numerical properties of Eqn. 28, but, in principle, it should provide an accurate method to generate on-the-fly polarization potentials for complex molecules whose polarizabilities are not well approximated by atom-site-based models. One possible failure in this approach is that the accuracy of the effective potential relies on the quality of the approximation to the true core-electron wavefunctions (since $|\phi\rangle$ is built from these orbitals), particularly given that first-order perturbation theory generally gives good energies but poor wavefunctions. An alternate approach would be to approximate the new pseudo-orbital by solving the eigenspectrum for Eqn. 16 and applying perturbation theory to this set of eigenfunctions. The method proposed above, however, minimizes the number of self-consistent equations that need to be solved and continues to avoid having to evaluate the computationally expensive two-electron terms. Once the perturbed pseudo-orbital is found, the effective potential can be computed using Eqn. 23. Of course, the formalism underlying Eqn. 27 applies to any perturbative field, not just electric polarization; thus, our formalism provides a straightforward and computationally efficient means of stepping outside the frozen-core approximation.

IV. CONCLUSIONS

In summary, we have presented an analytically exact reformulation of the Phillips-Kleinman pseudopotential theory. This formalism has the advantage of furnishing a clear geometric interpretation, but its real importance lies in its computational efficiency. We expect that the use of Eqns. 22 and 23 will allow the computation of complex pseudopotentials that can not be well represented by model potentials and that currently lie on the edge of computational practicality. In fact, computation of the pseudopotential for large molecules will no longer be limited by solving the iterative pseudopotential equation, but instead by the generation of the core-electron wavefunctions for large multi-electron systems. In the subsequent paper [17], we will apply our method to calculate the effective potential for and excess electron interacting with tetrohydrofuran (THF). This is now the largest molecule for which an exact pseudopotential has been calculated, and as discussed above, lies well on the low end of computational feasibility. We also intend to follow up on the use of this formalism to include molecular polarization in a more accurate manner.

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