Kohn-Sham density functional theory (KS-DFT) \cite{1, 2} is an efficient and usefully accurate electronic structure method, because it replaces the interacting Schrödinger equation with a set of single-particle orbital equations. Calculations with several hundred atoms are now routine, but there is always interest in much larger systems. Many such systems are treated by a lower-level method, such as molecular mechanics, but a fragment in which a chemical reaction occurs must still be treated quantum mechanically. A plethora of such QM/MM approaches have been tried and tested, with varying degrees of success\cite{3}. These are often combined with attempts at orbital-free DFT, which avoids the KS equations, but at the cost of higher error and unreliability.

On the other hand, partition theory (PT) \cite{4, 5} combines the simplicity of functional minimization with a density optimization to define fragments (such as atoms) within molecules, overcoming limitations of earlier approaches to reactivity theory \cite{6, 7}. While there are now many definitions of, e.g., charges on atoms, none have the generality of PT and the associated promise of unifying disparate chemical concepts. However, previous work on PT has been either formal\cite{1, 2} or for two atom systems\cite{3, 4}.

In this paper, we unite KS-DFT with PT to produce an algorithm that allows a KS calculation for a molecule to be performed via a self-consistent loop over isolated fragments. Such a fragment calculation exactly reproduces the result of a standard KS calculation of the entire molecule. We demonstrate its convergence on a 12-atom example. This also shows that fragments can be calculated 'on the fly', as part of solving any KS molecular problem.

Thus we present a formally exact framework within which existing practical approximations can be analyzed and, for smaller systems, compared with exact quantities. In practical terms, our method suggests new approximations that can, by construction, scale linearly\cite{10} with the number of fragments (so-called $O(N)$), and allow embedding of KS calculations within cruder force-field calculations (QM/MM). It also suggests ways to improve XC approximations so as to produce correct dissociation of molecules\cite{11}.

To understand the relation between DFT and PT, recall that the Hohenberg-Kohn theorem proves that for a given electron-electron interaction and statistics, the external (one-body) potential $v(r)$ is a unique functional of the density $n(r)$. The total energy can be written as:

$$E[n] = F[n] + \int d^3r \, n(r) \, v(r),$$

where $F[n]$ is a universal functional, defined by the Levy-Lieb constrained search\cite{12} over all antisymmetric wavefunctions $\Psi$ yielding density $n(r)$:

$$F[n] = \min_{\Psi \to n(r)} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle,$$

where $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic energy and Coulomb repulsion operators respectively. The KS equations are single-particle equations defined to reproduce $n(r)$. Define the KS energy as

$$E_{\Phi}[n] = \langle \Phi_s[n] | \hat{T} + \hat{V}_s | \Phi_s[n] \rangle = T_s[n] + \int d^3r \, n(r) \, v(r),$$

where $\hat{V}$ is the external potential operator, $\Phi_s[n]$ is the KS wavefunction (usually a single Slater determinant) of density $n(r)$, and $T_s[n]$ is the kinetic energy of $\Phi_s[n]$. Define the Hartree-exchange-correlation energy, as

$$E_{\text{HXC}}[n] = E[n] - E_{\Phi}[n],$$

so that the KS potential is $v(r) + v_{\text{HXC}}(r)$, where

$$v_{\text{HXC}}(r) = \delta E_{\text{HXC}}[n] / \delta n(r).$$
Partition theory deals with the problem of dividing a system into localized fragments. For molecules or solids,

\[ v(r) = \sum_{\beta} \frac{Z_{\beta}}{|r - R_{\beta}|} = \sum_{\alpha=1}^{N_f} v_\alpha(r), \]  

(6)

where \( Z_{\beta} \) is the atomic charge of a nucleus at point \( R_{\beta} \), and these are regrouped into \( N_f \) fragment potentials, \( v_\alpha(r) \). The fragmentation is chosen based on the particular use of PT: e.g., one might atomize an entire molecule, or merely separate off a well-known chemical species. The partition problem is then to divide \( n(r) \) between the fragments. There are many methods for doing so, but in PT\(^4\)\(^3\) we minimize the total fragment energy

\[ E_f = \min_{\{n_\alpha\}} \sum_{\alpha=1}^{N_f} \left( F[n_\alpha] + \int d^3r \ n_\alpha(r) v_\alpha(r) \right), \]  

(7)

where \( n_\alpha(r) \) is the density on the \( \alpha \)-th fragment. Each fragment is considered to be in contact with a distant reservoir of electrons\(^1\), so its integral \( N_\alpha \) need not be an integer. If \( N_\alpha = p_\alpha + \nu_\alpha \), with \( 0 \leq \nu_\alpha \leq 1 \), then

\[ F[n_\alpha] = (1 - \nu_\alpha)F[p_\alpha] + \nu_\alpha F[p_{\alpha+1}], \]  

(8)

and the integer densities are ground-states of a common potential. Minimizing the Lagrangian:

\[ \mathcal{G} = E_f + \int d^3r \ v_p(r) \left( n(r) - \sum_{\alpha=1}^{N_f} n_\alpha(r) \right), \]  

(10)

yields the correct fragment densities. The Lagrange multiplier \( v_p(r) \) is called the partition potential, and satisfies

\[ \frac{\delta F[n_\alpha]}{\delta n_\alpha(r)} + v_\alpha(r) + v_p(r) = \mu. \]  

(11)

So \( n_\alpha(r) \) is the ground-state density of \( N_\alpha \) electrons in effective fragment potential \( v_{f,\alpha}(r) = v_\alpha(r) + v_p(r) \).

Thus PT replaces a molecule of interacting fragments with an effective system of non-interacting fragments, and \( v_p(r) \) is the analog of \( v_{\text{HXC}}(r) \) in KS theory. Analogous to Eq. \(^4\), we define the partition energy as

\[ E_p[n_\alpha] = E[n] - E_f[n_\alpha], \]  

(12)

which, via Eq. \(^4\), is a functional of \( \{n_\alpha(r)\}_{\alpha=1...N} \). Functional differentiation yields:

\[ v_p(r) = \delta E_p[n_\alpha]/\delta n_\alpha(r). \]  

(13)

Analogous to KS-DFT, once \( E_p[n_\alpha] \) is given, we have a closed set of equations that yield the molecular density and energy at self-consistency. Next, we use a superscript 0 to denote quantities evaluated in the physical dissociation limit, where all bond lengths between fragments have been taken to \( \infty \) while keeping intrafragment distances fixed. In this limit, the fragments do not interact and their densities do not overlap, and \( E_f^{(0)} \) is the sum of the truly separated fragments, each with density \( n_\alpha^{(0)}(r) \).

Defining the relaxation energy \( E_{\text{rel}} = E_f^{(0)} - E_f \), we write

\[ E_p = E_{\text{dis}} + E_{\text{rel}}, \quad E_{\text{dis}} = E - E_f^{(0)}, \]  

(14)

where \( E_{\text{dis}} \) is the electronic contribution to the dissociation energy. Thus \( E_p < 0 \) for any bound molecule (by construction), is expected to be much smaller than the total energy (on the scale of chemical bonding), and vanishes as the fragments are pulled apart.

In a KS fragment calculation, the KS potential for the \( \alpha \)-th fragment is found from Eq. \(^4\) in KS quantities:

\[ v_{s,f,\alpha}[n_\alpha, \bar{n}_\alpha](r) = v_s[n_\alpha](r) + (v(r) + v_{\text{HXC}}[n](r) - v_s[n](r)), \]  

(15)

where \( v_s[n](r) = -\delta T_s[n]/\delta n(r) \), and \( n(r) = n_\alpha(r) + \bar{n}_\alpha(r) \). This is the central result of this paper, as it gives the fragment KS potential for a pair of trial densities, \( n_\alpha(r) \) and \( \bar{n}_\alpha(r) \), in terms of quantities from KS-DFT.

In Eq. \(^4\), \( v_s[n_\alpha](r) \) is simply the KS fragment potential from the previous iteration, but \( v_s[n](r) \) is the KS potential for a trial density for the whole molecule. Many methods exist for finding this\(^4\). We iterate\(^5\):

\[ v_s^{(m+1)}(r) = v_s^{(m)}(r) + \gamma \left[ n^{(m)}(r) - n^{(k)}(r) \right], \]  

(16)

where \( n^{(m)}(r) \) is the density found from potential \( v_s^{(m)}(r) \), \( \gamma > 0 \) is a constant, and \( n^{(k)}(r) \) is the target density (sum of fragment densities from the \( k \)-th PDFT iteration) whose KS potential we are trying to find. To find the

![FIG. 1: Solid line: The exact spin-unpolarized ground state of 12 electrons in the potential of Eq. \(^4\). Dashed lines: The fractionally occupied fragment densities. By symmetry, the other half of the density is simply the mirror image of that shown.](image-url)
fragments occupations, note that at self-consistency, the chemical potentials of all the fragments will be equal. We choose $N^{(k+1)}_\alpha = N^{(k)}_\alpha - \Gamma \left( \mu_\alpha^{(k)} - \bar{\mu}^{(k)} \right)$, where $\Gamma$ is another positive constant and $\bar{\mu}$ is the average of the fragment chemical potentials, used in conjunction with Eq. (8) for the functionals[26].

The starting point in PDFT is to solve the KS equations for each isolated fragment, generating their self-consistent densities $n^{(0)}_\alpha(r)$ and KS potentials, and a trial molecular density which is the sum of overlapping atomic densities. Then Eq. (10) is iterated to find its KS potential, which completes the inputs for Eq. (15), and the cycle repeated to self-consistency, when $E_{\text{dis}}$ is found by evaluating $E_\alpha$ on the final fragments, and subtracting the relaxation energies via Eq. (13).

To show that our algorithm converges, we performed a PDFT calculation on a 12-atom 1d chain with 12 spin-unpolarized non-interacting fermions, with potential:

$$v(x) = \frac{12}{\sum_{\alpha=1}^{12} \cosh^2 [x + \left( \alpha - 6.5 \right) R]} - 1.$$  \hspace{1cm} (17)

We chose complete atomization into 12 fragments, so we only ever solve one- or two-electron problems in a single well. Fig. 1 shows the atomic and molecular densities after convergence. The molecular density is identical to that found by direct solution of the eigenvalue problem for the entire molecule, and doubly occupying the first 6 eigenstates, which are delocalized over the entire molecule. We see a small alternation between higher and lower densities throughout the molecule. The fragment density occupations reflect this, being 0.77, 1.13, 0.98, 1.06, 1.02, 1.04 moving inwards towards the center of the chain. In Fig. 2 we show both the partition potential and effective fragment potential for the last atom. The (not very large) $v_p(r)$ polarizes the density toward the molecular center, and shifts the density inwards compared to a free atom. The partition potential continues throughout the whole chain, lowering each fragment potential in the bonding region between atoms. The depth of these troughs oscillates, reflecting the oscillation in occupations. In Fig. 3 we show the convergence of the occupation numbers to their final values, after some initial oscillations. The total energy of the molecular system can be found via Eq. 12. We find $E_f = -5.888$ and $E_p = -1.803$ leading to $E = -7.691$, which is exactly that of the direct solution. Since $E_f^{(0)} = -6$, $|E_{\text{rel}}| \ll |E_p| \ll |E|$, as expected.

Our calculation was in fact far more expensive than a regular KS calculation, because we invert the KS problem for each trial molecular density exactly. But the purpose here was not speed, but the calculation of exact partition potentials for small molecules and simple solids. It produces the exact partition potential corresponding to a given KS calculation for the molecule.

The many potential uses of PDFT are made clear by this example. In principle, Eq. (15) is exact, but requires the KS potential of the entire system and to deduce the energy at the end of the calculation, one needs

$$E_p = \Delta T_\alpha[n_\alpha] + \Delta E_{\text{hxc}}[n_\alpha] + \sum_{\alpha, \beta \neq \alpha}^{N_f} \int d^3 r \, n_\alpha(r) v_\beta(r),$$  \hspace{1cm} (18)

where $\Delta G[n_\alpha] = G[\sum n_\alpha] - \sum G[n_\alpha]$. However, any local-type approximation makes the method $O(N)$. Thus, all the attempts of orbital-free DFT, to find useful approximations to $\Delta T_\alpha[n]$, have now a simple framework in which to be tested[16]. Moreover, there are no formal difficulties arising from taking density variations within a fixed density, as the trial molecular density is simply the sum of the fragment densities, which are varied freely. Although the exact fragment $T_\alpha$ and $v_\alpha(r)$ would be known during a calculation, approximations for $\Delta T_\alpha$ would take full advantage of any cancellation of errors. For embedding calculations, a simple approximation would be to...
treat the system plus some fraction of its environment (a border region) exactly, and all the rest approximately. Since the KS potential is typically near-sighted, such a scheme should converge rapidly.

For the dissociation of molecules, one can also see how to ensure correct dissociation energies within PDFT: simply constrain occupations to be those of the isolated fragments. For \( \text{H}_2 \), we constrain the spin occupations on the fragments to be (0,1) and vice versa. Of course, this is what happens when symmetry is broken as the bond is stretched, and the difficulty is in producing a scheme that seamlessly goes over to \((1/2,1/2)\) occupations as \(R\) reduces to the equilibrium value. The value of our formalism is that it produces a framework for both addressing these questions and constructing approximate solutions.

There is a simple adiabatic connection formula for PDFT. Consider scaling all bond lengths between fragments by \(\lambda^{-1}\) (again keeping intrafragment densities fixed), where \(0 < \lambda \leq 1\). For each \(\lambda\), we find those molecular densities whose fragment densities match those of our molecule, and define the corresponding partition energy, \(E_p(\lambda)\). At \(\lambda = 1\), we have the original molecule; as \(\lambda \to 0\), the bonds become large and the fragments do not interact, so that \(E_p(0) = 0\). For intermediate \(\lambda\), the molecular density is simply that of the fragments, overlapped a distance \(R/\lambda\) apart. Then

\[
E = E_f + \int_0^1 d\lambda \frac{dE_p(\lambda)}{d\lambda}.
\]  

This allows all the methods of traditional intermolecular symmetry-adapted perturbation theory (SAPT)\([17]\) to be applied to this problem, but with the advantage that the fragment densities remain fixed. Interestingly, because the fragments will generally have dipole moments, the partition energy decays as \(1/R^3\), so that the integrand above behaves as \(\lambda^2\). (For physical systems that are well-separated and have attractive van der Waals forces, such effects must be cancelled by analogous terms in \(E_{\text{rel}}\).

There has been considerable previous work on schemes designed to allow a fragment calculation of a larger molecule, either within the framework of orbital-free DFT or atomic deformation potentials, sometimes producing the same (or similar) equations. Among the earliest, Cortona’s crystal potential (later called embedding potential)\([18, 19]\) is an intuitive prescription for \(v_p(r)\). But our formalism reproduces the exact solution of the original problem, using only quantities that are already defined in KS-DFT. For example, this is not possible in general without the ensemble definition of Eq. \(5\), which produces the correct self-consistent occupations (unlike, e.g., the self-consistent atomic deformation method\([20, 21]\), where this choice leads to a basis set dependence\([22]\)). We also never freeze the total density\([22, 24, 25]\), but only ever consider it as a sum of fragment densities. This avoids ever needing density variations that are limited by some frozen total density, which produces bizarre functional derivatives, different from those of KS DFT. None of these issues arise once smooth (e.g. local or gradient-corrected) approximations are made to the kinetic energy functional\([18, 19, 21]\), but they are vital in a formally exact theory. Thus the present PDFT can be regarded as a formal exactification (and therefore justification) of these pioneering works.

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