

Partition density-functional theory

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Partition density functional theory is a formally exact procedure for calculating molecular properties from Kohn-Sham calculations on isolated fragments, interacting via a global partition potential that is a functional of the fragment densities. An example is given and consequences discussed.

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Kohn-Sham density functional theory (KS-DFT) [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 (MM), but a fragment in which a chemical reaction occurs must still be treated quantum mechanically (QM). A plethora of such QMMM approaches have been tried and tested, with varying degrees of success [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) [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 [6,7]. While there are many definitions of charges on atoms, few have the generality of PT and the associated promise of unifying disparate chemical concepts, as is illustrated in Refs. [8] and [9].

In this Brief Report, 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, as we demonstrate 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. Our method suggests new approximations which could, by construction, scale linearly [10] with the number of fragments [so-called $O(N)$], allow embedding of KS calculations within cruder force-field calculations (QMMM), and even improve exchange-correlation (XC) approximations so as to produce correct dissociation of molecules [11].

In Ref. [12], we presented the basic equations of PDFT and their application to a two-electron model system, for

which the inversion of the KS equations is trivial. But here we develop and apply PDFT fragment calculations for more than two electrons, where the inversion must be performed via a self-consistent procedure, and also determine fractional charges self-consistently. We regard the present calculation as a demonstration of the ability of a many-electron PDFT fragment calculation to exactly reproduce the results of the corresponding molecular calculation.

The Hohenberg-Kohn theorem [2] states that, for N electrons, the ground-state energy of a given external (one-body) potential $v(\mathbf{r})$ can be found by minimizing

$$E_v[n] = F[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}), \quad (1)$$

where $n(\mathbf{r})$ is a trial electron density and $F[n]$ is a functional defined by the Levy-Lieb constrained search [13] over all antisymmetric wave functions Ψ yielding $n(\mathbf{r})$:

$$F[n] = \min_{\Psi \rightarrow n(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle, \quad (2)$$

where \hat{T} and \hat{V}_{ee} are the kinetic energy and Coulomb repulsion operators, respectively. The KS equations [1] are single-particle equations defined to reproduce $n(\mathbf{r})$. Define the KS energy as

$$E_{s,v}[n] = T_s[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}), \quad (3)$$

where $T_s[n]$ is the kinetic energy of the KS orbitals. The Hartree-exchange-correlation energy, is then

$$E_{\text{HXC}}[n] = E_v[n] - E_{s,v}[n], \quad (4)$$

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

$$v_{\text{HXC}}(\mathbf{r}) = \delta E_{\text{HXC}}[n] / \delta n(\mathbf{r}). \quad (5)$$

Partition theory deals with the problem of dividing a system into localized fragments. For molecules or solids,

$$v(\mathbf{r}) = \sum_{\beta} \frac{Z_{\beta}}{|\mathbf{r} - \mathbf{R}_{\beta}|} = \sum_{\alpha=1}^{N_f} v_{\alpha}(\mathbf{r}), \quad (6)$$

where Z_β is the atomic charge of a nucleus at point \mathbf{R}_β , and these are regrouped into N_f fragment potentials, $v_\alpha(\mathbf{r})$. 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 $n(\mathbf{r})$ between the fragments, which is done by [4,5] minimizing the sum of fragment energies, while ensuring the sum of fragment densities matches the molecular density:

$$E_f = \min_{\{n_\alpha\}} \left\{ \sum_{\alpha=1}^{N_f} E_{v_\alpha}[n_\alpha] \left\| \sum_{\alpha=1}^{N_f} n_\alpha(\mathbf{r}) = n(\mathbf{r}) \right. \right\}, \quad (7)$$

where $n_\alpha(\mathbf{r})$ is a density of the α th fragment.

Each fragment is in contact with a distant reservoir of electrons [14], so its integral N_α need not be an integer. If $N_\alpha = p_\alpha + \nu_\alpha$, p_α an integer and $0 \leq \nu_\alpha \leq 1$, then [14]

$$F[n_\alpha] = (1 - \nu_\alpha) F[n_{p_\alpha}] + \nu_\alpha F[n_{p_\alpha+1}], \quad (8)$$

where

$$n_\alpha(\mathbf{r}) = (1 - \nu_\alpha) n_{p_\alpha}(\mathbf{r}) + \nu_\alpha n_{p_\alpha+1}(\mathbf{r}), \quad (9)$$

and the integer densities are ground states of a common potential.

To establish a set of effective *noninteracting* fragments, we define the partition energy functional as

$$E_{p,\{\nu_\alpha\}}[\{n_\alpha\}] = E_v[n] - \sum_{\alpha=1}^{N_f} E_{v_\alpha}[n_\alpha] \quad (10)$$

analogous to Eq. (4). Since $\delta F[n_\alpha]/\delta n_\alpha(\mathbf{r}) + v_{f,\alpha}(\mathbf{r}) = \mu$ at a minimum, we find that each minimizing $n_\alpha(\mathbf{r})$ is the ensemble ground-state density of an *effective* fragment potential,

$$v_{f,\alpha}(\mathbf{r}) = v_\alpha(\mathbf{r}) + v_p(\mathbf{r}), \quad v_p(\mathbf{r}) = \left. \frac{\delta E_p[\{n_\alpha\}]}{\delta n_\alpha(\mathbf{r})} \right|_{\min}. \quad (11)$$

Thus PT maps a problem of interacting fragments into an effective isolated fragment problem, just as the KS scheme [1] maps the interacting electronic problem into a noninteracting one.

Now consider a modern KS DFT calculation of the molecule, using some approximation for XC in Eq. (4). Writing Eq. (10) in terms of KS quantities, and functionally differentiating

$$v_p(\mathbf{r}) = v(\mathbf{r}) + v_{\text{HXC}}[n](\mathbf{r}) - v_s[n](\mathbf{r}) - v_\alpha(\mathbf{r}) - v_{\text{HXC}}[n_\alpha](\mathbf{r}) + v_s[n_\alpha](\mathbf{r}), \quad (12)$$

where $v_s[n](\mathbf{r}) = -\delta T_s[n]/\delta n(\mathbf{r})$. Each fragment can be solved using KSDF, where the KS equation is

$$\left\{ -\frac{1}{2} \nabla^2 + v_{s,f,\alpha}[n_\alpha, \bar{n}_\alpha](\mathbf{r}) \right\} \phi_j(\mathbf{r}) = \epsilon_j \phi_j(\mathbf{r}), \quad (13)$$

and $v_{s,f,\alpha}(\mathbf{r})$ is the *effective* KS potential of the α th fragment, found by adding $v_{\text{HXC}}[n_\alpha](\mathbf{r})$ to Eq. (11). Using Eq. (12), it may be written as

$$v_{s,f,\alpha}[n_\alpha, \bar{n}_\alpha](\mathbf{r}) = v_s[n_\alpha](\mathbf{r}) + \{v(\mathbf{r}) + v_{\text{HXC}}[n](\mathbf{r}) - v_s[n](\mathbf{r})\}, \quad (14)$$

where $\bar{n}_\alpha(\mathbf{r}) = n(\mathbf{r}) - n_\alpha(\mathbf{r})$. This central result gives the fragment KS potential for a pair of trial densities, $n_\alpha(\mathbf{r})$

and $\bar{n}_\alpha(\mathbf{r})$, in terms of quantities from KS-DFT. At self-consistency, Eq. (14) becomes a tautology, where only the first potential remains. Similar expressions arise in density embedding [15–22], but do not necessarily define fragments that exactly reproduce the molecular density of an approximate KS calculation.

The natural starting point of PDFT is to solve the KS equations for each isolated fragment, generating their self-consistent KS potentials, densities $n_\alpha^{(0)}(\mathbf{r})$, and overlapped sum $n^{(0)}(\mathbf{r})$. These are fed into Eq. (14) to produce a new set of KS fragment potentials, and the procedure repeated until self-consistency is reached. To illustrate, we performed a PDFT calculation on a 12-atom 1d chain with 12 spin-unpolarized noninteracting fermions, with potential

$$v(x) = \sum_{\alpha=1}^{12} \frac{-1}{\cosh^2[x + (\alpha - 6.5)R]}. \quad (15)$$

Atomic units are used throughout the illustration. We chose complete atomization, so no fragment ever contains more than two electrons. To find $v_{s,f,\alpha}^{(k+1)}(\mathbf{r})$ in Eq. (14), we know $v_s[n_\alpha^{(k)}](\mathbf{r})$ from the previous iteration, but $v_s[n^{(k)}](\mathbf{r})$ is the KS potential for a *molecular* trial density, $\sum n_\alpha^{(k)}(\mathbf{r})$. To find this [23], we iterate [24]

$$v_s^{(p+1)}(\mathbf{r}) = v_s^{(p)}(\mathbf{r}) + \gamma[n^{(p)}(\mathbf{r}) - n^{(k)}(\mathbf{r})], \quad (16)$$

where $n^{(p)}(\mathbf{r})$ is the density found from potential $v_s^{(p)}(\mathbf{r})$, $\gamma > 0$ is a constant. This internal iteration is more expensive than a single KS calculation, because we invert the KS problem for each trial molecular density *exactly*. (Our aim is not speed, but to reproduce the *exact* molecular density.) To find the fragment occupations within the PDFT iteration, note that at self-consistency, the chemical potentials of all the fragments are equal, so choose $N_\alpha^{(k+1)} = N_\alpha^{(k)} - \Gamma(\mu_\alpha^{(k)} - \bar{\mu}^{(k)})$, where Γ is another positive constant and $\bar{\mu}$ is the average of the fragment chemical potentials, used in conjunction with Eq. (8) for the functionals [25].

Figure 1 shows the atomic and molecular densities after convergence. The molecular density is identical to that found

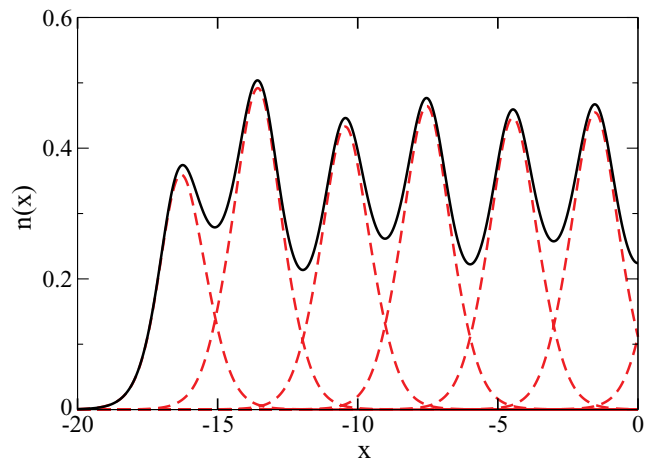


FIG. 1. (Color online) Solid line: The exact spin-unpolarized ground state of 12 electrons in the potential of Eq. (15). Dashed lines: The fractionally occupied fragment densities. By symmetry, the other half of the density is simply the mirror image of that shown.

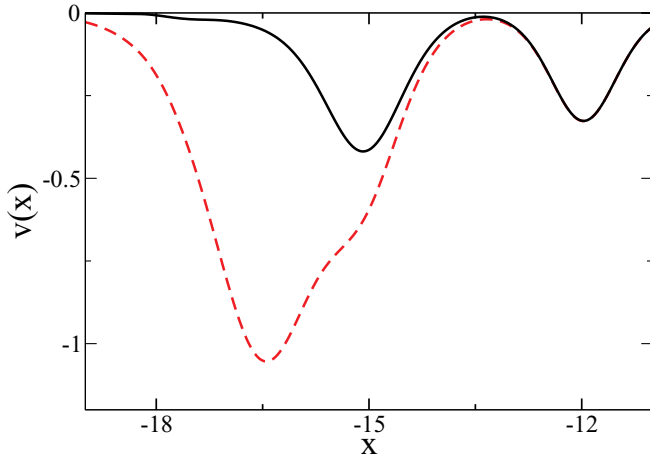


FIG. 2. (Color online) The exact partition potential (solid line) for the atomized chain and the fragment potential for the last atom (dashed line). The ground state with an occupation of 0.77 in this potential can be seen as the end fragment density in Fig. 1.

by direct solution of the eigenvalue problem for the entire molecule, and doubly occupying the first six 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 inward toward 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) $v_p(\mathbf{r})$ polarizes the density toward the molecular center, and shifts the density inward 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 fluctuations.

Many features of PDFT are illustrated by our example. First, the total energy of the molecule need *never* be calculated, so that dissociation energies are found directly, not as the difference of two huge numbers. To see this, define a relaxation

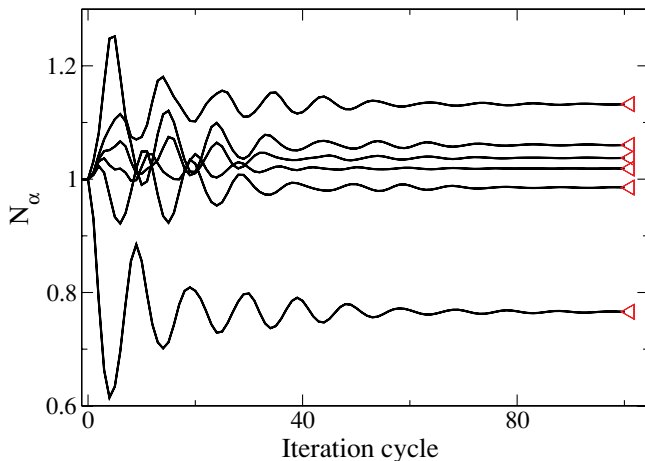


FIG. 3. (Color online) The convergence of the fragment occupation values, N_α , during an exact PDFT calculation.

energy (similar to the promotion energy of Ref. [26]): $E_{\text{rel}} = E_f^{(0)} - E_f$, so that

$$E_p = E_{\text{dis}} + E_{\text{rel}}, E_{\text{dis}} = E - E^{(0)}, \quad (17)$$

where E_{dis} is the electronic contribution to the dissociation energy, which is negative for a bound molecule. But $E_f^0 \leq E_f$ because the isolated fragment energy is the minimum in Eq. (7) *without* constraint, so $E_p < 0$. Since the fragment densities will only be slightly distorted relative to the free fragments, $|E_{\text{rel}}|$ should be small, so that E_p should be comparable to E_{dis} . In our example, $E_f = -5.888$ and $E_p = -1.803$ leading to $E = -7.691$, exactly that of the direct solution. Since $E_f^{(0)}$ is -6 , $|E_{\text{rel}}| \ll |E_p| \ll |E|$.

Secondly, Eq. (14) is exact, but taking practical advantage of PDFT requires some approximation (analogous to approximating XC in the KS scheme). The exact partition energy requires the molecular kinetic energy:

$$E_p = \Delta T_s[n_\alpha] + \Delta E_{\text{HXC}}[n_\alpha] + \sum_{\alpha, \beta \neq \alpha}^{N_f} \int d^3r n_\alpha(\mathbf{r}) v_\beta(\mathbf{r}), \quad (18)$$

where $\Delta G[n_\alpha] = G[\sum n_\alpha] - \sum G[n_\alpha]$. Although the exact fragment T_s and $v_s(\mathbf{r})$ would be known during a calculation, approximations for ΔT_s would take full advantage of any cancellation of errors (analogous to LDA for XC). Any local-type approximation, such as finding $v_s[n](\mathbf{r})$ using only the fragment's density plus that of its neighbors, should make the method $O(N)$. All attempts of orbital-free DFT to find useful approximations to $\Delta T_s[n]$ have now a simple framework in which to be tested [27]. 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. 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. Our example suggests that fractional electron transfer is vital (more important than changes in normalized densities), but must be accounted for in any accurate embedding scheme.

Thirdly, 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 H_2 , we constrain the spin occupations on the fragments to be 0 and 1. 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.

Finally, there is a simple adiabatic connection formula for PDFT. Consider scaling all bond lengths between fragments by λ^{-1} (keeping intrafragment densities fixed), where $0 < \lambda \leq 1$. For each λ , 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 $\lambda \rightarrow 0$, the bonds become large and the fragments do not interact, so that $E_p(0) = 0$.

For intermediate λ , the molecular density is simply that of the fragments, overlapped a distance R/λ apart. Then

$$E = E_f + \int_0^1 d\lambda \frac{dE_p(\lambda)}{d\lambda}. \quad (19)$$

This allows all the methods of traditional intermolecular symmetry-adapted perturbation theory (SAPT) [28] 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 λ^2 . (For physical systems that are well separated and have attractive van der Waals forces, such effects must be canceled 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) [15,16] is an

intuitive prescription for $v_p(\mathbf{r})$. 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. (8), which produces the correct self-consistent occupations (unlike, e.g., the self-consistent atomic deformation method [17,18], where this choice leads to a basis set dependence [19]). We also never freeze the total density [20–22], 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 [15,16,18], but they are vital in a formally exact theory. Thus the present PDFT can be regarded as a formal generalization of these pioneering works.

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