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Density Functional Partition Theory with Fractional Occupations

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Abstract: Partition theory (PT) is a formally exact methodology for calculating the density of any molecule or solid via separate calculations on individual fragments. Just as Kohn–Sham density functional theory (DFT) introduces noninteracting fermions in an effective potential that is defined to yield the exact density of the interacting problem, in PT a global effective potential is found that ensures that the sum of the fragment densities is that of the full system. By combining the two, density functional partition theory (DFPT) produces a DFT scheme that yields the (in principle) exact molecular density and energy via Kohn–Sham calculations on fragments. We give the full formalism and illustrate DFPT in the general case of noninteger fragment occupations.

1. Introduction

In the world of electronic structure, molecules and solids are typically considered in one of two distinct ways. In the first, the system is treated as a whole, and molecular orbitals (or Bloch wave functions for bulk crystals) are calculated. These are solutions of some effective potential theory, such as Kohn–Sham density functional theory^{1,2} or Hartree–Fock,^{3,4} and often describe the system well near equilibrium geometries. The major difficulty is then finding usefully accurate approximations to the total energy. In the second view, one considers isolated atoms as the starting point, and then relatively weak interactions between such units. This view appears necessary for strongly correlated solids such as NiO, strongly correlated molecules such as Cr₂, or any molecule as its bonds are stretched. In such cases, standard approximations for the single-reference approach usually fail, often quite completely. Thus, in practice, the worlds of weak- and strong-correlation have divided.⁵

In previous work,⁶ we showed that the partition theory in ref 7 plays a role analogous to that of the Kohn–Sham (KS) formalism in density functional theory (DFT). In Kohn–Sham theory,² a reference system is created which is much easier to solve and in which the interactions between electrons have been turned off. In partition theory,^{7,8} the reference system has been constructed from isolated effective fragments (e.g., atoms) between which there are no interactions. In both theories, the total electronic density of the system is used as the connection between the reference and reality; it remains unchanged from one to the other and so uniquely defines the reference. Many other analogies are made within the paper. Suffice it to say that, just as KS DFT is particularly well-suited to weakly correlated systems, partition theory is well suited, though not limited to, weakly interacting fragments. We illustrate our method with an analysis of a system of two electrons moving independently in a simple one-dimensional potential. In ref 6, a model calculation was shown in which only integer particle numbers occurred, as determined by symmetry. Just as in pure partition theory, much more is gained in going from that case⁹ to the asymmetric case,¹⁰ leading to fractional occupations. Unlike in ref 6, here, we perform a calculation with

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noninteger occupations, which is the more general case that will be encountered in molecular calculations.

We start with the relevant background information on DFT, including the KS scheme and how partition theory can be used to break a system into fragments. Following this, we review density functional partition theory (DFPT) before generalizing the analysis of ref 6. Next, we perform a DFPT calculation on a one-dimensional model system of a heteronuclear diatomic molecule, leading to fractionally occupied fragments, before we conclude with a discussion of significance.

2. Background

In this section, we review both Kohn–Sham DFT and partition theory, highlighting the analogies between them.

2.1. Kohn–Sham Density Functional Theory. In the KS² approach to DFT, one constructs a set of noninteracting equations:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r})\right]\phi_j(\mathbf{r}) = \varepsilon_j\phi_j(\mathbf{r}) \quad (1)$$

where the orbitals $\phi_j(\mathbf{r})$ are defined to reproduce the exact density, $n(\mathbf{r})$, of the interacting system of interest. The KS potential $v_s(\mathbf{r})$ is unique via the Hohenberg–Kohn theorem.¹ The total energy is then rewritten in terms of the reference system:

$$E[n] = T_s[n] + U[n] + E_{\text{XC}}[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \quad (2)$$

where T_s is the KS kinetic energy, U the Hartree energy, E_{XC} the unknown XC energy, and $v(\mathbf{r})$ the one-body external potential. The (in principle exact) total energy can be found by solving eq 1 and inserting the resulting density in the expression above, eq 2. The most important result of ground-state DFT is that the KS potential of eq 1 is given by

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{XC}}(\mathbf{r}) \quad (3)$$

where

$$v_{\text{H}}[n](\mathbf{r}) = \frac{\delta U[n]}{\delta n(\mathbf{r})} = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (4)$$

is the Hartree potential and

$$v_{\text{XC}}[n](\mathbf{r}) = \frac{\delta E_{\text{XC}}[n]}{\delta n(\mathbf{r})} \quad (5)$$

is the XC potential. Thus, if one knows E_{XC} as a density functional, a closed set of self-consistent equations results, which can be solved for any system. With good approximations to $E_{\text{XC}}[n]$, this scheme has proven useful in many applications.¹¹

2.2. Partition Theory. On the other hand, partition theory⁷ provides a method for breaking a system into a sum of fragments. Begin from the one-body potential, $v(\mathbf{r})$, which is typically a sum of contributions, most from individual nuclei, for example,

$$v(\mathbf{r}) = - \sum_{\beta} \frac{Z_{\beta}}{|\mathbf{r} - \mathbf{R}_{\beta}|} \quad (6)$$

where Z_{β} is the atomic charge of a nucleus at point \mathbf{R}_{β} . In partition theory, we group these contributions into N_f fragments of our choosing:

$$v(\mathbf{r}) = \sum_{\alpha=1}^{N_f} v_{\alpha}(\mathbf{r}) \quad (7)$$

and each $v_{\alpha}(\mathbf{r})$ is the sum over one or more nuclei. The simplest possible choice is to divide the system into two parts ($N_f = 2$), which we call binary fragmentation. These parts would obviously be the two nuclei in a diatomic molecule but could also be the nuclei of a chemical group extracted from a large molecule, or those of a molecule interacting with a surface. One can imagine many cases for which that could prove useful; two examples can be seen in Figure 1. An alternative choice is atomization, in which every term in eq 6 above is separated, and the number of fragments matches the number of nuclei.

Once the fragments have been picked, the partition problem is to find fragment densities $n_{\alpha}(\mathbf{r})$ such that they add to the total molecular density:

$$\sum_{\alpha=1}^{N_f} n_{\alpha}(\mathbf{r}) = n(\mathbf{r}) \quad (8)$$

Within partition theory, this is done by minimizing the total energy of the independent fragments, E_f , with the constraint that the sum of the fragment densities must match the molecular density, that is, eq 8. The total energy of the fragments is

$$E_f = \sum_{\alpha=1}^{N_f} \varepsilon_{\alpha} \quad (9)$$

where ε_{α} is the energy of each fragment. Since there is no constraint that a fragment's particle number, N_{α} , be an integer, the Perdew, Parr, Levy, and Balduz (PPLB) formulation^{12,13} is used. Thus

$$\varepsilon_{\alpha} = (1 - \nu_{\alpha})E_{\alpha}[n_{p_{\alpha}}] + \nu_{\alpha}E_{\alpha}[n_{p_{\alpha}+1}] \quad (10)$$

where $E_{\alpha}[n]$ is the energy density functional for each fragment α . The fragment particle number is $N_{\alpha} = p_{\alpha} + \nu_{\alpha}$, p_{α} and $p_{\alpha} + 1$ are the lower and upper bordering integers of N_{α} , and $0 \leq \nu_{\alpha} < 1$. The PPLB scheme is simply that of the fragment in contact with an infinite but distant reservoir.

We note the following:

- If all fragments are separated from each other, these fragment densities become exactly those of the isolated fragments, $n_{\alpha}^{(0)}(\mathbf{r})$.

- One solves the Hamiltonian for each isolated fragment independently of the other fragments. It is the sum of these fragment energies that is minimized.

- It may appear that finding the minimum requires first solving for the molecular density and, so, is even more work than solving the initial problem. But an exactly analogous statement can be made about KS DFT, whose true value is

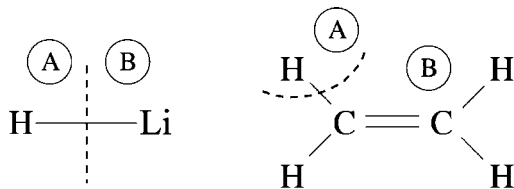


Figure 1. Two examples of binary fragmentation into fragments A and B. The figure on the left shows a lithium hydride molecule at equilibrium bond length, while on the right, an ethene molecule is shown with one substituent cornered off as one of two fragments. Due to the lack of symmetry, in both cases, the fragments will have noninteger occupations at equilibrium bond lengths.

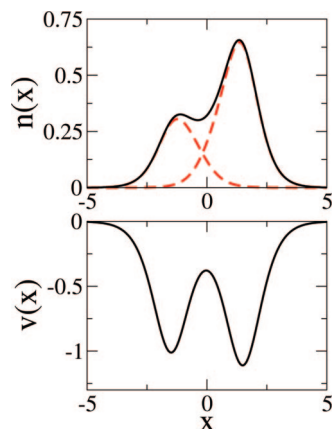


Figure 2. Top panel: The exact density (solid line) for two noninteracting fermions in the potential defined in eq 26 with $R = 3$ and shown below. The two exact partition densities (dashed lines) for this system. Bottom panel: The corresponding molecular potential (solid line) as defined in eq 26.

only apparent when approximations are made. Below, we show the same thing for partition theory.

The process of finding the minimum produces an extremely useful conceptual tool. Minimizing the Lagrangian:

$$\mathcal{G} = E_f - \mu \left(\sum_{\alpha=1}^{N_f} N_{\alpha} - N \right) + \int d^3r v_p(\mathbf{r}) \left(\sum_{\alpha=1}^{N_f} n_{\alpha}(\mathbf{r}) - n(\mathbf{r}) \right) \quad (11)$$

where $N_{\alpha} = \int d^3r n_{\alpha}(\mathbf{r})$, yields the solution to the partition problem.⁷ The Lagrange multiplier μ is identified as the chemical potential of the molecule,⁸ while the Lagrange multiplier that constrains the sum of the fragment densities to be the molecular density is a potential, dubbed the partition potential, $v_p(\mathbf{r})$. This is a global property of the molecule, uniquely defined once we have chosen a particular fragmentation. It has the interesting aspect that, when added to any fragment potential, the sum is exactly that potential for which the fragment density is a ground-state density. In the upper panel of Figure 2, the exact total density for a model system is shown. It is the solution for two noninteracting fermions in the potential shown in the lower panel of Figure 2 and is discussed in detail later, in the illustration. Solving the partition problem yields the two fragment densities, which are also shown in the upper panel of Figure 2. It can be seen that adding these two fragment densities will give the

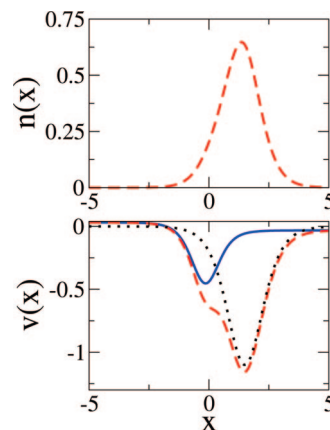


Figure 3. Top panel: The fragment density (dashed line) for the B atom of Figure 1. Bottom panel: The exact partition potential $v_p(x)$ (solid line) for this system, the nuclear potential $v_B(x)$ (dotted line), and the fragment potential $v_B(x) + v_p(x)$ (dashed line). This potential has the fragment density shown in the upper panel as its ground-state density, and the same is true for the A atom.

total density. In the lower panel of Figure 3, we show the exact partition potential for this problem. When added to a fragment potential, it gives an effective potential for each fragment; this is shown as the dashed line in the lower panel of Figure 3. The ground-state density of this effective potential can be seen in the upper panel of Figure 3, it is exactly the same as the fragment density shown in the upper panel of Figure 2.

We emphasize here that, once a choice of fragmentation has been made, the entire procedure is then unambiguously defined and leads to unique densities. The user chooses fragments depending on which aspects they wish to study, usually guided by chemical intuition.

The conceptual structure of partition theory has deep roots, going back to Moffitt's proposed solution of the atoms in molecules (AIM) problem, the ultimate partition into "atoms".¹⁴ Some of the fundamental concepts of partition theory were introduced by Parr et al.¹⁵ in prescient work which reformulated the AIM problem within the framework of DFT. They introduced three central ideas:

1. The electron density of a molecule should be decomposed *exactly* into a sum of contributions from individual atoms.
2. This decomposition should be made unique by minimizing the *promotion energy*, the increase of the sum of the energies (the density functionals) of the individual atoms caused by meeting constraint 1.
3. The electron numbers on the individual atoms need not be integers.

Palke¹⁶ applied these ideas to an analysis of the H_2 molecule. Building upon the Parr et al. work, Guse¹⁷ developed the conceptual structure further, carrying out a Legendre transformation on the sum of the atomic energies before the minimization, thereby introducing a Lagrange parameter without recognizing explicitly that it plays the role of an external potential, which is the same for all of the atoms. Rycklewski and Parr¹⁸ reformulated the theory in terms of wave functions. Ayers and Parr¹⁹ recognized that

the atoms in the molecule were changing in response to an effective external potential in a significant contribution to chemical reactivity theory, but that potential was not identified with Guse's Lagrange multiplier. Perdew et al. (PPLB)^{12,13} constructed a rigorous generalization of DFT for noninteger systems, and Parr²⁰ used its conceptual structure only to give physical meaning to the notion that atoms-in-molecules could have noninteger electron numbers. Thus, several of the essential elements of the conceptual structure of partition theory had been present in the literature for two decades before the current formulation.⁷

3. Density Functional Partition Theory

In this section, we expand upon the methodology developed in ref 6, which allows one to *calculate a molecular density and energy from individual calculations on fragments* via a self-consistent loop. In this sense, it is the analog of the KS method, in which the energy is found from self-consistent calculations on noninteracting electrons. Clearly, such a capability could in general have tremendous significance for many areas of current research, from $O(N)$ scaling to quantum mechanics/molecular mechanics (QM/MM) methods.

To do so, think of the total fragment energy, eq 9, as analogous to the sum of orbital energies in KS theory. Then, define the partition energy as

$$E_p = E - E_f \quad (12)$$

analogous to the Hartree-XC energy in KS theory. If $E_f^0 = \sum_{\alpha} \epsilon_{\alpha}^0$ is the total energy of the isolated fragments, then we can write

$$E_p = E_{\text{dis}} + E_{\text{rel}} \quad (13)$$

where E_{rel} is the fragment relaxation energy (the promotion energy¹⁵):

$$E_{\text{rel}} = E_f^0 - E_f = \sum_{\alpha=1}^{N_f} \Delta \epsilon_{\alpha} = \sum_{\alpha=1}^{N_f} (\epsilon_{\alpha}^0 - \epsilon_{\alpha}) \quad (14)$$

and $E_{\text{dis}} = E - E_f^0$ is the dissociation energy. For any bound molecule, $E_{\text{dis}} < 0$. Furthermore, since ϵ_{α}^0 is the ground-state energy for the isolated fragment and ϵ_{α} is an expectation value of the same Hamiltonian, $\Delta \epsilon_{\alpha} \leq 0$ always. Thus, $E_p < 0$. Note that these energies are typically much smaller than total electronic energies and vanish as the molecule is stretched.

We can consider the partition energy as a functional, $E_p[\{n_{\alpha}\}]$, of the fragment densities alone for the given external potential and choice of fragmentation. We now examine the effect of making small variations in one fragment density, $\delta n_{\alpha}(\mathbf{r})$, to the partition energy. The first term of eq 13 is the ground-state energy of the system relative to that of the isolated parts, so variations in the density are zero because we are at its minimum. For E_{rel} , the second term, only the α th fragment energy changes. Since the fragment density minimizes the α th fragment in the presence of $v_p(\mathbf{r})$, then $v_p(\mathbf{r}) = -\delta \epsilon_{\alpha} / \delta n_{\alpha}(\mathbf{r})$, so that

$$v_p(\mathbf{r}) = \frac{\delta E_p[\{n_{\alpha}\}]}{\delta n_{\alpha}(\mathbf{r})} \quad (15)$$

that is, given any expression for $E_p[\{n_{\alpha}\}]$, we can extract the corresponding partition potential, $v_p(\mathbf{r})$, and then calculate new fragment densities, which are then used to generate a new partition potential, and so on. Thus, approximating $E_p[\{n_{\alpha}\}]$ produces a closed loop, and a direct scheme for doing a DFPT calculation. The steps of a DFPT calculation are as follows:

(1) Guess the fragment densities $\{n_{\alpha}\}$. A reasonable first guess would be $\{n_{\alpha}^0(\mathbf{r})\}$, the densities of the isolated fragments. This naturally leads to integer occupations, usually those of the neutral fragmentations.

(2) Construct the partition potential, $v_p(\mathbf{r})$, using eq 15.

(3) Solve for each $n_{\alpha}(\mathbf{r})$ in its respective fragment potential $v_{\alpha}(\mathbf{r}) + v_p(\mathbf{r})$, retaining the values of the fragment occupations, $\{N_{\alpha}\}$.

(4) Cycle steps 2 and 3 until self-consistency, and evaluate E_f .

(5) Repeat with small changes of the occupation numbers, and continue to find the lowest value of E_f .

(6) Along with the fragment densities, this yields the total molecular density and the molecular energy (via $E = E_f + E_p$).

This is the method we have used in our illustration, and it is guaranteed to yield the molecular density and energy, once self-consistent potentials can be found at each value of the occupations. In a larger calculation, it would be optimum to take variations in the fragment occupations also and find both occupations and potentials simultaneously self-consistently.

In principle, any electronic-structure method can be used to calculate the fragments. However, in practice, most of such methods will not provide a way to functionally differentiate the corresponding E_p . Even within KS DFT, one does not usually know the noninteracting kinetic energy, T_s , as a functional of the density. Only with an explicit density functional can the corresponding derivative needed for the partition potential be taken.

To derive the expression for $v_p(\mathbf{r})$ in DFPT, we begin with the universal functional, defined via the Levy constrained search:^{21,22}

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{\text{ee}} | \Psi \rangle \quad (16)$$

Then, the ground-state energy of any density is given by

$$E[n] = F[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \quad (17)$$

where $v(\mathbf{r})$ is its corresponding one-body potential. Thus,

$$\epsilon_{\alpha} = F[n_{\alpha}] + V_{\alpha}[n_{\alpha}] \quad (18)$$

where, for simplicity, we assume N_{α} is an integer; otherwise, eq 10 must be used. Thus, E_p is

$$E_p[n] = F[n] - \sum_{\alpha=1}^{N_f} F[n_{\alpha}] + \sum_{\alpha=1}^{N_f} \sum_{\beta \neq \alpha}^{N_f} \int n_{\alpha}(\mathbf{r}) v_{\beta}(\mathbf{r}) \quad (19)$$

Now

$$\frac{\delta F[n]}{\delta n_{\alpha}(\mathbf{r})} = \frac{\delta F[n]}{\delta n(\mathbf{r})} = \mu - v(\mathbf{r}) \quad (20)$$

and

$$\frac{\delta F[n_{\alpha}]}{\delta n_{\alpha}(\mathbf{r})} = \mu - v_{\alpha}(\mathbf{r}) - v_{\text{p}}(\mathbf{r}) \quad (21)$$

so we can write the partition potential in terms of functional derivatives of the universal functional:

$$v_{\text{p}}(\mathbf{r}) = \frac{\delta F[n]}{\delta n(\mathbf{r})} - \frac{\delta F[n_{\alpha}]}{\delta n_{\alpha}(\mathbf{r})} + \sum_{\beta \neq \alpha}^{N_{\text{f}}} v_{\beta}(\mathbf{r}) \quad (22)$$

This gives an expression for $v_{\text{p}}(\mathbf{r})$ for each of the N_{f} fragments. From eqs 17 and 2, the universal functional can be decomposed into $F[n] = T_{\text{S}}[n] + U[n] + E_{\text{XC}}[n]$, leading to

$$v_{\text{p}}[\{n_{\alpha}\}](\mathbf{r}) = \frac{\delta T_{\text{S}}[n]}{\delta n(\mathbf{r})} - \frac{\delta T_{\text{S}}[n_{\alpha}]}{\delta n_{\alpha}(\mathbf{r})} + v_{\text{XC}}[n](\mathbf{r}) - v_{\text{XC}}[n_{\alpha}](\mathbf{r}) + \sum_{\beta \neq \alpha}^{N_{\text{f}}} (v_{\beta}(\mathbf{r}) + v_{\text{H}}[n_{\beta}](\mathbf{r})) \quad (23)$$

for any α and using the fact that the Hartree potential is linear in $n(\mathbf{r})$. Explicit density functional expressions are needed for both $T_{\text{S}}[n]$ and $E_{\text{XC}}[n]$. However, since the expression only depends on differences between the functional derivatives of these, some of the error due to approximating these may cancel.

We point out that DFPT is close in spirit (not in execution) to previous work by other authors. Cortona's crystal potential (called embedding potential by later workers)^{23,24} is analogous to our $v_{\text{p}}(\mathbf{r})$, but the procedure for finding it is distinct from the variational framework of DFT. And, he does not provide an explicit functional for it. Wesolowski and Warshel²⁵ gave an explicit form to it and applied it to a two-part system instead of a crystal, with solvation effects specifically in mind. Carter and collaborators^{26,27} applied these ideas to adsorbates on and defects in metals, giving a functional form for the embedding potential that is formally equal to ours but has quite a different interpretation. We highlight six key features of DFPT: (1) We can break the system up into an arbitrary number of fragments. (2) We do not suppose that the densities of the parts can be varied independently when their densities are constrained to add to the density of the whole. (3) We obtain the partition potential as a Lagrange multiplier, which allows relaxation of the constraint in a variational procedure that lies outside the pre-established domain of DFT. (4) Our partition potential acts on all parts and is the same for all. (5) We achieve electronegativity equalization through the use of PPLB. (6) We do not fix the density of any part of our system. All fragment densities are self-consistent with respect to one another.

4. Illustration

In ref 6, we illustrated DFPT on a model system of a homonuclear diatomic molecule. We found, as expected, that

DFPT gave exactly the right energy and density. While this demonstrated the principle of DFPT, a more powerful example of its usefulness and relevance to real systems is a heteronuclear diatomic molecule. Unlike the symmetric case, the covalently bonded fragments will contain fractional numbers of electrons, necessitating the use of the PPLB formalism.¹² In partition theory, the AB heteronuclear system has been studied¹⁰ for insight into molecular dissociation.

For one- or two-electron systems, the kinetic energy density functional is given exactly by the von Weizsäcker functional:

$$T_{\text{W}}[n] = \frac{1}{8} \int d^3r \frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})} \quad (24)$$

and if we study noninteracting fermions, then $E_{\text{p}}[n]$ as a density functional is known exactly. Taking the functional derivative with respect to a fragment density yields the partition potential, which for a binary fragmentation of a system is

$$v_{\text{p}}(\mathbf{r}) = v_{\text{B}}(\mathbf{r}) + \left(\frac{n^2(\mathbf{r})}{8n^2(\mathbf{r})} - \frac{n''(\mathbf{r})}{4n(\mathbf{r})} \right) - \left(\frac{n_{\text{A}}'^2(\mathbf{r})}{8n_{\text{A}}'^2(\mathbf{r})} - \frac{n_{\text{A}}''(\mathbf{r})}{4n_{\text{A}}(\mathbf{r})} \right) \quad (25)$$

and vice-versa for the A fragment. If we work in one dimension, then the fragments can be solved for easily.

For this example, we use a $1/\cosh^2(x)$ potential for each "nucleus", giving the total potential for a diatomic system with separation R as

$$v(x) = v_{\text{A}}(x) + v_{\text{B}}(x) = -\frac{1}{\cosh^2(x + R/2)} - \frac{1.1}{\cosh^2(x - R/2)} \quad (26)$$

Here, the A fragment plays the role of a Lewis base, while B is a Lewis acid. The small difference in nuclear charges is chosen so as to mimic the effect of screening in an interacting system. The total particle number is two, allowing us to use the von Weizsäcker functional even when fractional charges are present.²⁸

The minimization of the Lagrangian, eq 11, in the partition problem is over both the density $n_{\alpha}(x)$ and the occupation N_{α} . As described above, we find self-consistent solutions for fixed values of N_{α} . In Figure 4, we plot the molecular energy found after three iteration cycles for five occupation numbers. We can clearly see that there is a minimum at $N_{\text{A}} = 0.655$, and in fact, it is already extremely close to the exact molecular energy. The convergence for the other occupation numbers is very slow, but the minimum at $N_{\text{A}} = 0.655$ remains even after 10 iteration steps. For practical calculation, the occupancy may be set on the fly, but for the purposes of this demonstration, this procedure is sufficient.

To see how the density converges for each iteration, we will use the final occupation $N_{\text{A}} = 0.655$ from now on. In Figure 5, we show the convergence for one of the two fragment densities for this problem, through several self-consistency cycles. The total potential is the same as that shown in the lower panel of Figure 2, while the two fragment

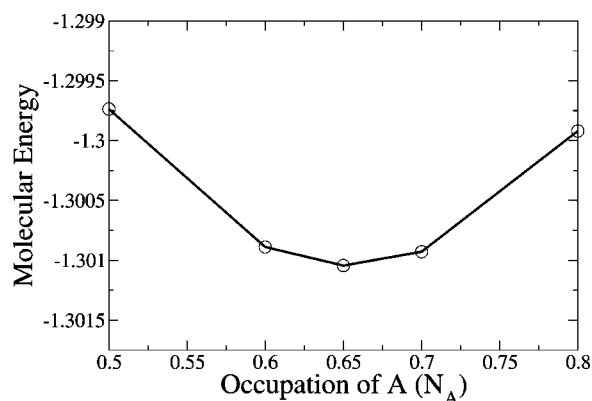


Figure 4. The molecular energy after three iteration cycles as a function of the fractional occupation of the A fragment (N_A) used in each DFPT calculation. The occupation on B is thus $2 - N_A$. The initial fragment densities are the same for each calculation and are simply those of the respective free fragments. The minimum occurs at $N_A = 0.655$, which is then the occupation used in all subsequent calculations.

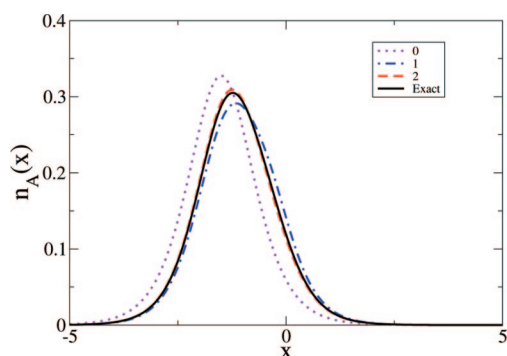


Figure 5. The density for the left (A) fragment as defined by eq 26 with $R = 3$ for the first three self-consistency cycles, labeled 0, 1, and 2, respectively. Also shown is the exact fragment density. Even after just two cycles, the fragment density is almost on top of the exact density, on this scale. For more self-consistency steps, it continues converging toward the exact answer. Calculations were performed using three-site finite difference formulas for derivatives and 2001 grid points with a grid spacing of 0.013 au.

potentials, $v_A(x)$ and $v_B(x)$, are given in eq 26 with $R = 3$. For the initial fragment densities (cycle 0), we use the densities for the two isolated fragments. We then use these to construct a partition potential from eq 25, which is then used to construct effective fragment potentials, $v_\alpha(x) + v_p(x)$. If we then solve for each fragment density in this new potential, we find the cycle 1 density, shown as the dotted–dashed line in Figure 5. It can be seen that the density for this fragment has been shifted toward the other “nucleus”, as compared to the isolated case. This is due to the partition potential lowering the fragment potential, v_A , so as to move density into the bonding region, as would be expected.

In Figure 6, the solid line is the total molecular density, found by directly solving for two noninteracting fermions in total potential $v(x)$. It is the same as that shown in Figure 2. In both this case and for the fragments, the density is found by solving the Schrödinger equation numerically on a real-space grid. Derivatives of the density are found using a finite-difference scheme. If we sum the A fragment density shown

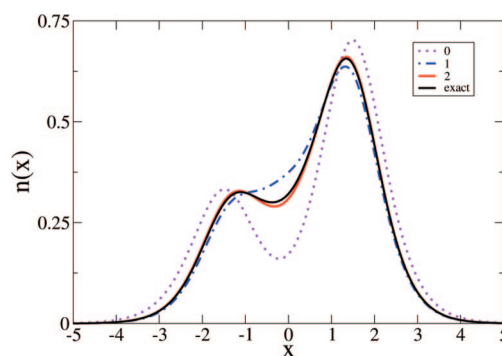


Figure 6. Molecular densities for various cycles 0, 1, and 2 of the self-consistency calculation for this system. Also shown is the exact density for the full system. The density after just two cycles is very close to the exact density, and after three cycles it cannot be distinguished from the exact density on this scale. Convergence continues as more cycles are added, as can be seen in Figure 7.

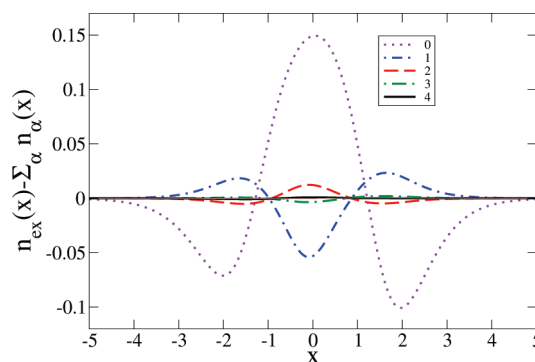


Figure 7. Difference between the exact molecular density, $n_{\text{ex}}(x)$, and the sum of the fragment densities for each self-consistency cycle of the DFPT calculation. It is the difference between each of the DFPT densities in Figure 6 and the exact density. After each cycle, this difference decreases, and the convergence to the exact answer is clear.

in Figure 5 with its counterpart on B at each iteration step, we find the corresponding molecular density. These are plotted in Figure 6, and it can be seen that the density at each self-consistency cycle is converging to the exact answer. The convergence toward the exact molecular density can be seen more clearly in Figure 7, where we show the density differences from the overlapped “atomic” densities. We add in the results for more iteration steps, and it is clear that the error decreases with every iteration.

The energy of the molecule may also be calculated using eq 12 for each set of fragment densities. Again, we see the calculation converge to the exact energy of -1.30106 . The energy of the initial guess was -1.26067 , while after three cycles, it was -1.30104 , essentially converged for this level of calculation.

5. Significance

We have demonstrated that, with an explicit expression for the partition energy functional E_p , a self-consistent DFPT calculation can be performed on fragments and that the result converges to the molecular answer. Unlike ref 6, here the fragments have noninteger occupations. The fragments are

solved individually, which, for large interacting systems, would greatly reduce computational cost.

One may wonder, what is the point of our methodology? After all, in order to find the partition potential exactly, we need to know the functional for the entire problem, so we have saved nothing. The point is that one can construct simple approximations to the partition energy as a functional of the fragment densities, which will yield new and different approximations to the many-atom problem. In principle, one can even apply a high-accuracy quantum chemical method to the solution for a fragment and, via an approximate partition functional, embed that solution in the entire molecule (QM/MM). Another useful possibility is to perform, for example, a molecular mechanics simulation and then use overlapped atomic densities in an approximate partition potential to apply to the fragment of interest, where accurate energy differences are needed. Work is ongoing to explore the most useful approximations in different situations.

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