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Application of partition density-functional theory to one-dimensional models

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We have carried out calculations for one-dimensional model systems using the self-consistency algorithm of the recently published partition density-functional theory. The issues of uniqueness of occupation numbers and a relation to the self-consistent atomic deformation model are addressed. Possibilities for obtaining more accurate representations of the kinetic-energy functional and its potential are discussed.

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I. INTRODUCTION

The most efficient methods for application of density-functional theory (DFT) need more accurate expressions of the kinetic-energy functional T_k to achieve accuracy in total energy comparable to results obtained by the method of Kohn and Sham [1]. Elliott *et al.* [2], hereafter referred to as EBCW, have proposed a "formally exact procedure," called partition DFT (PDFT), for defining fragments of a larger problem. They illustrate their method for noninteracting electrons in a one-dimensional model potential and emphasize that they obtain "correct" occupation numbers for electrons on the various fragments. We find that this result comes with a caveat, described in Sec. II. Nevertheless, the partition theory (PT) iteration method produces a unique result for the total-kinetic-energy functional and its functional derivative that may be useful for deriving specific approximations to it. This is discussed in Sec. III, where we relate the PDFT method to the self-consistent atomic deformation (SCAD) method of Boyer *et al.* [3]. In Sec. IV we discuss problems associated with approximating the kinetic-energy functional using data for both T_k and its functional derivative.

II. PDFT CALCULATIONS IN ONE DIMENSION

For our discussion of the PDFT method, we rewrite equations from the EBCW paper in a simplified, less general manner, sufficient for one-dimensional models with potentials given by

$$v(x) = \sum_{i=1}^{N_w} v_i(x - x_i) \tag{1}$$

in Hartree atomic units, where, in general, N_w is an even number of identical potential wells spaced such that $v(x) = v(-x)$. To illustrate the PDFT method EBCW chose $N = 12$ noninteracting electrons bound by $N_w = 12$ wells of the form $v_i(x) = -1/\cosh^2(x)$, with $|x_i - x_{i-1}| = 3$.

The PT iteration method determines fragment potentials $v_{f,i}$ using Eq. (14) in EBCW,

$$v_{f,i}^{(k+1)}(x) = v_{-W}\big[n_i^{(k)}(x)\big] + v(x) - v_{-W}^{(L)}(x), \tag{2}$$

Eq. (16) in EBCW,

$$v_{-W}^{(l+1)}(x) = v_{-W}^{(l)}(x) + \gamma[\eta^{(l)}(x) - n^{(k)}(x)], \tag{3}$$

and an equation in the text following Eq. (16) in EBCW,

$$N_i^{(k+1)} = N_i^{(k)} - \Gamma\big(\mu_i^{(k)} - \bar{\mu}^{(k)}\big). \tag{4}$$

Here $v_{-W} = -\delta T_W[n]/\delta n$ is the negative of the functional derivative of the Weizsäcker kinetic energy, $n_i^{(k)}$ is the number density for N_i electrons on the ith fragment, obtained by solving Schrödinger's equation for the potential $v_{f,i}^{(k)}(x)$, and $\eta^{(l)}(x)$ is the number density for $N = \sum N_i$ electrons bound by the potential $v_{-W}^{(l)}(x)$. The v_{-W} terms in Eq. (3) are so labeled only because the l iterations are *started* using the $-W$ potential; specifically, $v_{-W}^{(l)}(x) = v_{-W}[n^{(k)}(x)]$ for $l = 1$, where $n^{(k)} = \sum_i n_i^{(k)}$ is obtained from the solutions of Schrödingers' equations for the kth set of fragment potentials [Eq. (2)]. As long as $N_i \leqslant 2$ the correct kinetic-energy functional is the Weizsäcker form. In Eq. (4) $\mu_i^{(k)}$ is the eigenvalue of Schrödinger's equation for the kth potential of the ith fragment, and $\bar{\mu}^{(k)}$ is the average of the N_w fragment eigenvalues. The overall convergence is governed by the number of k and l iterations (K and L) and the values of parameters Γ and γ. As K and L become large, this PT iteration method yields $v_{-W}^{(L)}(x) \to v(x) + C$, where C is a constant, and $\eta^{(L)}(x) \to n^{(K)}(x)$, the exact number density for the molecule, a remarkable result. EBCW also stress that this method provides unique, correct, and exact results for n_i and N_i, a point that requires further discussion.

Using a simple Runge-Kutta-based algorithm to solve Schrödinger's equation for the total and fragment potentials, we were able to repeat the results of EBCW for the $N = N_w = 12$ model. Obtaining the exact total energy necessitates using the kinetic energy produced by solving Schrödinger's equation for the potential from $v_{-W}^{(L)}$. We find that convergence of the total energy takes place very slowly with increasing L. Specifically, $L \sim 100$ is needed to obtain accuracy in the total energy to within ∼0.001. Doubling L approximately halves the error, so $L \sim 800$ is needed to reduce the error to ∼0.0001.

After many attempts to reproduce the EBCW results, we noticed that the N_i are unique if the potentials resulting from Eq. (2) are each shifted so that they approach zero for large $|x|$. This does not happen automatically because the Weizsäcker

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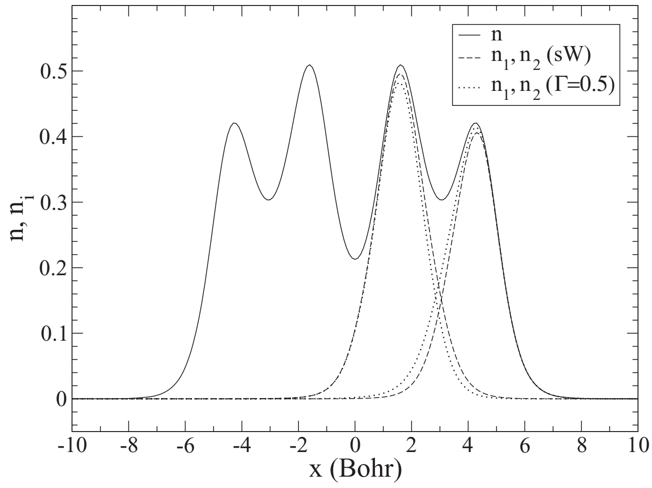

FIG. 1. Total density and fragment densities obtained for $N_w = 4$ by the PDFT method using shifted and unshifted Weizsäcker potentials (sW and $\Gamma = 0.5$)

potential generally approaches a nonzero constant value for large $|x|$. While we see no physical reason to make this shift, we found it necessary to reproduce the EBCW results. If they are not so shifted, then N_i converge to other values that depend on the choice of Γ. Nevertheless, the central result of convergence of the sum of the fragment densities to the exact total density remains valid. In fact, we find that convergence to the same level of accuracy in the total energy is achieved in less than half as many k iterations using unshifted potentials. Results for n and n_i shown in Fig. 1 were obtained using shifted. Weizsäcker potentials, labeled sW, and unshifted potentials, labeled by the value of Γ used. Both calculations produce the same $n(x)$, different occupation numbers notwithstanding: $N_1 = 0.955$ and 0.865, respectively, for $\Gamma = 0.5$ and sW. We obtain $N_1 = 0.931$ using $\Gamma = 1.0$ in a non-sW calculation. The differences are more apparent in the fragment potentials $v_{f,i}$, as illustrated in Fig. 2 for the $i = 2$ well of the $N_w = 4$ model.

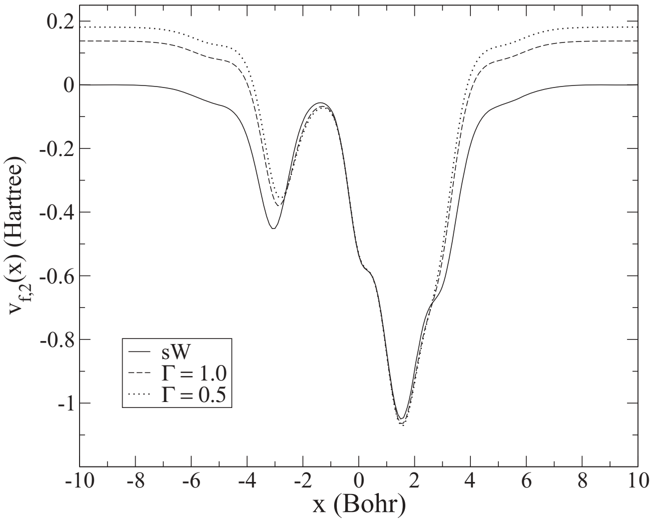

FIG. 2. Fragment potentials for $i = 2$ and $N_w = 4$ obtained using sW, $\Gamma = 1.0$, and $\Gamma = 0.5$ calculations.

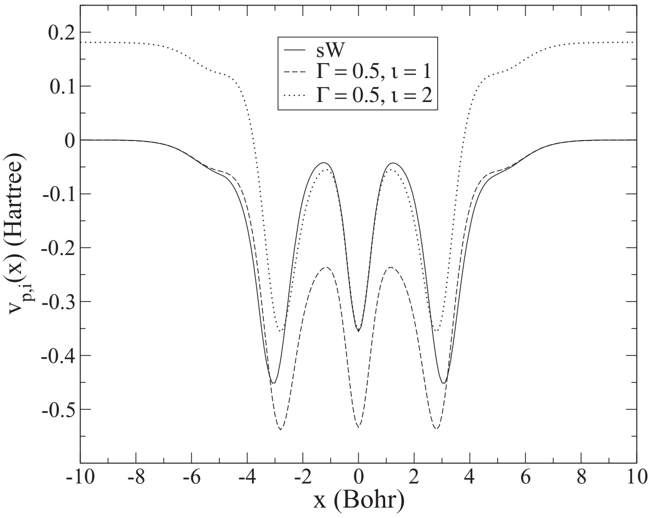

FIG. 3. Partition potentials $v_{p,i}$ for $N_w = 4$ obtained using sW and $\Gamma = 0.5$ calculations.

In an sW calculation all of the converged fragment potentials $v_{f,i}$ contain a contribution that is the same for all fragments, dubbed the partition potential. Noting that $v_{-W}^{(L)}(x) \to v(x) + C$ and $v_{-W}[n_i^{(K)}(x)]$ differ from zero at large $|x|$ by the same constant C, Eq. (12) of EBCW simplifies to

$$v_{p,i}(x) = v_{f,i}(x) - v_i(x). \tag{5}$$

In a non-sW calculation the partition potentials for any given pair of sites differ by only a constant value that depends on the specific pair and the value of Γ. This is illustrated in Fig. 3, where $v_{p,i}$ is plotted as a function of x for the two types of calculations. Since the large $|x|$ values of n and n_i are nearly the same for the outermost wells ($i = 1$ and $i = N_w$), the first and third terms of Eq. (2) nearly cancel for large $|x|$. Hence, $v_{p,1}$ is approximately zero at large $|x|$, as seen in Fig. 3. Clearly, the differences between sW-v_p and Γ-$v_{p,i}$ are more than just constant shifts.

It may appear that the uncertainty in the occupation numbers could be eliminated by selecting two wells per fragment. Then, perhaps, N_i would be two for all fragments. We have verified this is the case for our model with $N_w = 8$ when the non-sW method is used. Assuming two electrons per fragment, the non-sW calculation yields energy levels of -0.673 and -0.518 (-0.674 and -0.527) for $i = 1$ ($i = 2$), implying that our assumption of $N_i = 2$ was correct. And we note that since $N_i = 2$ for all i, the results do not depend on the value of Γ.

However, if we attempt to perform the same calculation using the sW approach, then the PT method does not converge. The problem results because the second eigenvalue of fragment $i = 2$ decreases to the point of going below the first eigenvalue of $i = 1$, implying a need to put more than two electrons on the $i = 2$ fragment, tending to spoil the Weizsäcker approximation for this fragment. Nevertheless, if we continue to employ the Weizsäcker potential for the $i = 2$ density, then even an infinitesimal amount of charge moved to the new lower-level state produces a finite change in the large-$|x|$ Weizsäcker potential, and the resulting W shift moves the second eigenvalue of the $i = 2$ fragment well above that of the first level of $i = 1$ fragment. After a few more iterations the levels again try to cross, and the cycle repeats *ad infinitum*.

While application of the sW-PT method does produce unique N_i values for the models with one well per fragment, we believe it is wrong to say they are "correct" values or the PDFT method is "formally exact." The uniqueness results from the unphysical shift of the Weizsäcker potentials so they approach zero as $|x| \to \infty$.

Attempts to determine overlapping-fragment models should strive to select fragments that have either empty or fully occupied levels, permitting a straightforward calculation of dipole moments and polarization [4]. If such is not possible, then either the model is flawed, or it models a metallic-like system that conducts electricity by moving electrons from one site to another.

III. PDFT AND SCAD

We write Eqs. (4) and (5) of the SCAD expression [3] of DFT,

$$T[n(x)] = \sum_i T_0[n_i(x)] + T_k[n(x)] - \sum_i T_k[n_i(x)] \tag{6}$$

and

$$v_{f,i}(x) = v(x) + v_k[n(x)] - v_k[n_i(x)], \tag{7}$$

for this one-dimensional model. Here, $T_0[n_i(x)]$ is the kinetic energy derived from Schrödinger's equation for $v_{f,i}$, and T_k is some approximation to the kinetic-energy functional. If T_k were the exact kinetic-energy functional, then the first and third terms of Eq. (6) cancel.

We have compared SCAD to PDFT calculations for one-dimensional models assuming Bose, rather than Fermi, occupation. In this case, $T_k = T_W$. Naturally, SCAD and PDFT produce the same results for total energy and n_i, whether or not sW is employed. Specifically, sW-SCAD gives the same results as sW-PDFT, and non-sW-SCAD gives the same results as non-sW-PDFT. Like the Fermi-occupation calculations, results for fragment densities and occupation numbers differ between sW and non-sW, and for non-sW calculations they depend on the value of Γ. Of course, the convergence problem we found for the sW method with two wells per fragment is no longer a problem because, with Bose particles, only the lowest energy level is occupied. Finally, we note that the first and third terms of Eq. (6) exactly cancel (term by term for each i), and their sums are equal, except for the sign, to the value of the second term.

Previous applications of SCAD employed the Thomas-Fermi approximation, $T_k = T_{TF}$. In principle, the accuracy of SCAD could be improved by making better approximations for T_k and/or choosing overlapping molecular, rather than atomic, fragments. Application of SCAD to the water molecule [5] assumed three fragments, one for each nucleus. Numerous sets of orbitals for the hydrogen site were tested. In all cases, the SCAD method gave five energy levels for the oxygen site lower than the lowest level obtained for the hydrogen site. In other words, the three-site SCAD model for the water molecule naturally yields an O^{2-} ion in the potential of two protons. Consequently, no error results from overlapping electrons due to an inadequate T_k because there are no overlapping electrons. We believe it is misleading for EBCW to imply that occupations used in the SCAD model are chosen by the user. Technically, the user could change the water molecule occupations by making a *radical* change in basis functions, for example, by removing all orbitals originating on the oxygen site. Obviously, trying to supplement the loss by adding basis functions to the hydrogen sites would not be practical.

IV. APPROXIMATING T_k

We have attempted to determine approximations for T_k that would be suitable for application of SCAD to electrons in the one-dimensional model of Eq. (1). It turns out to be fairly easy to come up with formulas that include local and/or nonlocal terms which give a good approximation to the exact results for kinetic-energy density. However, in many cases, problems with convergence revealed that the kinetic-energy density could be well represented, while the potentials, derived from functional derivatives of T_k, were not. This led us to consider using PT-determined fragment potentials to help develop and test approximations for T_k. On the other hand, it is not clear how to do this because, as we have seen, fragment potentials depend on how the PT method is employed.

Another approach results from Eq. (3), which is the crux of the PT method. Recall that the $l = 1$ potential is $v_{-W}[n]$ and $v^{(L)}_{-W}(x)$ is, to within a constant, the external potential. In other words, the potential resulting from the difference between $T_k[n]$ and the Weizsäcker contribution is the external potential (to within a constant) minus the potential resulting from the Weizsäcker contribution. The constant, which originates from $v^{(l=1)}_{-W}[n]$, is canceled by that in $-v^{(L)}_{-W}(x)$. Thus, considering only Eq. (3), which is all about solving Schrödinger's equation for the molecule, leads to

$$v_u[n] = -v_W[n] - v^{(L)}_{-W}, \tag{8}$$

where v_u is the functional derivative of $T_u = T_k - T_W$.

V. SUMMARY

Results of calculations performed for one-dimensional model systems using the PDFT method imply that, in general, it does not decompose the charge density into correct or formally exact fragments. We were unable to reproduce the occupation numbers reported by EBCW unless we artificially shifted (sW) the Weizsäcker potentials to approach zero for large $|x|$. Non-sW calculations for models with two-well fragments gave unique results with two electrons per fragment, while the sW method produced artificial shifts in eigenvalues that prevented the PDFT algorithm from converging.

In principle, the SCAD method would be exact if T_k were exact, as was noted above for Bose occupation. In practice, SCAD calculations can benefit from PDFT in two ways. First, non-sW calculations can guide selection of optimum-sized fragments, as was noted for the example above which suggested using two-well fragments. Use of two-well fragments would likely reduce SCAD errors resulting from approximations for T_k. On the other hand, we do not consider fragments determined from sW calculations to be a reliable improvement. Second, the PT method can be used to obtain important data for use in determining better approximations for T_k.

Our attempts to find more accurate formulations for T_k point out the need to include data for $\delta T_k/\delta n$ in the fitting procedure. Snyder *et al.* [6] have emphasized this point using a machine learning approximation. Data for $\delta T_k/\delta n$ are obtained from the PDFT method by making changes in potential values proportional to charge-density differences [Eq. (3)].

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