

Comment on “Application of partition density-functional theory to one-dimensional models”

Peter Elliott,¹ Daniel Jensen,² Adam Wasserman,^{3,2} and Kieron Burke⁴

¹Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany

²Department of Physics, Purdue University, 525 Northwestern Ave., West Lafayette IN 47907, USA

³Department of Chemistry, Purdue University, 560 Oval Dr., West Lafayette IN 47907, USA

⁴Departments of Physics and of Chemistry, University of California, Irvine, CA 92697, USA

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Partition density-functional theory is a formally exact method for solving the ground-state electronic structure problem. It operates by dividing the system into non-interacting fragments along with a global effective potential, which, when solved to self-consistency, yields the exact energy and density (as the sum of the fragment densities) of the interacting system. A recent paper [L. L. Boyer and M. J. Mehl, Phys. Rev. A **86**, 012504 (2012)] questions the uniqueness of the fragment occupations and fragment densities. We demonstrate that their analysis is incorrect. We describe some of the technical details of partition density-functional calculations and discuss the relationship to other embedding schemes.

Spurred on by increasing computational resources, researchers are performing *ab-initio* electronic structure calculations for ever larger systems. In particular, density functional theory (DFT) has emerged as the preferred method for such simulations, by combining a reasonable level of accuracy with a reasonable computational time. However, even with advances in computing power, many systems remain beyond the capabilities of such calculations. Attempting to fill this gap are fragmentation methods[1, 2], embedding methods[3–12], or divide-and-conquer schemes[13, 14], all of which seek favorable scaling with system size without sacrificing the accuracy needed for useful results. Partition density functional theory (PDFT) was introduced[15] as a formally exact approach to this problem.

PDFT is build upon Partition Theory[16–18], in that when iterated to self-consistency it reproduces a Partition Theory (PT) calculation. Since PT is a well-defined partitioning scheme based on rigorous theorems, PDFT also shares this property. Reference 19 (hereafter labeled as BM) attempted to use PDFT for several model systems and found results inconsistent with what was claimed in Ref. 15. We note that the authors of BM *were* able to reproduce the PDFT calculations of Ref. 15, but with, from their point of view, an additional caveat. We will demonstrate that this caveat is unnecessary and hence the criticisms of PDFT in BM, all of which stem from this misunderstanding, are invalid.

The structure of this comment is as follows: we first state the foundations of PDFT; for a more detailed look we recommend the original paper[15] or any of the subsequent papers[20–24], however we will take this opportunity to explore certain practical aspects of PDFT in more detail. The review will also emphasize particular features of PDFT which are missing in the calculations in BM. We then discuss the criticisms of PDFT made in BM, demonstrating that their results are based on a flawed implementation of PDFT, and providing the correct PDFT results for their calculations.

Partition Theory addresses the problem of dividing up a given density $n(\mathbf{r})$ into separate pieces assigned to fragments within the full system. The particular choice of fragmentation is given by the user, whereby the separate nuclear potentials comprising the full system molecular potential $v(\mathbf{r})$, are grouped into fragments (labeled by α):

$$v(\mathbf{r}) = \sum_{\alpha} v_{\alpha}(\mathbf{r}) . \quad (1)$$

The set of fragment densities, $\{n_{\alpha}\}$, is then given by those which minimize the total fragment energy E_f , as defined by

$$E_f[\{n_{\alpha}\}] = \sum_{\alpha} E_{v_{\alpha}}[n_{\alpha}] \quad (2)$$

with the constraint that the sum of the fragment densities be equal to the full molecular density:

$$\sum_{\alpha} n_{\alpha}(\mathbf{r}) = n(\mathbf{r}) , \quad (3)$$

where $E_{v_{\alpha}}$ is the energy functional for potential v_{α} . Note that the fragment occupations, N_{α} (i.e. the integral of the fragment density) need not be integers, and so the energy functional for each fragment, $E_{v_{\alpha}}[n]$, utilizes the PPLB[25] formalism. Thus Partition Theory uniquely defines partition densities and occupations for a given problem. As a consequence of the constraint Eq. (3), each fragment density is the ground-state of the fragment potential $v_{f,\alpha}(\mathbf{r}) = v_{\alpha}(\mathbf{r}) + v_p(\mathbf{r})$, where $v_p(\mathbf{r})$ is the partition potential and is common to all fragments (i.e. a global potential). It can be shown that the partition potential is the functional derivative of the partition energy, $E_p[n] = E_v[n] - E_f[\{n_{\alpha}\}]$, i.e.

$$v_p(\mathbf{r}) = \frac{\delta E_p[n]}{\delta n_{\alpha}(\mathbf{r})} . \quad (4)$$

The purpose of EBCW was then to extend PT to a self-consistent DFT. This is analogous to extending the fact

that a Kohn-Sham non-interacting system can be defined for a given interacting density to create a self-consistent procedure for obtaining said density. Thus we utilize the density functional for $E_p[n]$ for sets of trial fragment densities, iterating until we reach the exact answer (i.e., that from a PT calculation). In EBCW (Eq. (12)), the expression for the partition potential during the iteration cycle was written in a compact form:

$$v_p(\mathbf{r}) = v(\mathbf{r}) + v_{\text{HXC}}[n](\mathbf{r}) - v_s[n](\mathbf{r}) - v_\alpha(\mathbf{r}) - v_{\text{HXC}}[n_\alpha](\mathbf{r}) + v_s[n_\alpha](\mathbf{r}) \quad (5)$$

where $v_s[n](\mathbf{r})$ is the Kohn-Sham potential for a given density. In Eq. 23 of Ref. 20, this is written as

$$v_p(\mathbf{r}) = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} - \frac{\delta T_s[n_\alpha]}{\delta n_\alpha(\mathbf{r})} + v_{\text{XC}}[n](\mathbf{r}) - v_{\text{XC}}[n_\alpha](\mathbf{r}) + \sum_{\beta \neq \alpha} (v_\beta(\mathbf{r}) + v_{\text{H}}[n_\beta](\mathbf{r})) \quad (6)$$

where we use the Euler equation, $\delta T_s[n]/\delta n(\mathbf{r}) = \mu - v_s[n](\mathbf{r})$, to go between the various expressions. As noted in previous work[24], at self-consistency this is not a problem. However, during the iteration cycle, more care must be taken.

At this point, we emphasize that the PDFT calculation must reproduce the PT result, so the quantity $v_p(\mathbf{r})$ must be a global potential. In Eq. (4), it might appear that each fragment would yield a different partition potential, but the beauty of PT is that each fragment density gives the same potential, the partition potential. However during the iteration cycle, this need not be true and as stated above, more care must be taken, the details of which we will discuss below.

Finally to complete the foundations of PDFT, the fragment occupations must be discussed. In principle, one could search over all sets of occupations, solving the PDFT equations for each set, and finding the set that minimizes the total fragment energy. In EBCW, we proposed a more efficient approach where the occupations are set *on-the-fly* during the iteration cycle using the equation $N_\alpha^{(k+1)} = N_\alpha^{(k)} - \Gamma(\mu_\alpha^{(k)} - \bar{\mu}^{(k)})$ where N_α is the fragment occupation, μ_α is the chemical potential of the fragment, $\bar{\mu}$ is the average of all the fragment chemical potentials, Γ is a positive constant, and k labels the iteration number. Thus at self-consistency all fragments have the same chemical potential, as they should do in PT, and explaining why using the Euler equation above did not alter the equations. For this particular method of finding the fragment occupations, it is essential that the partition potential at each iteration cycle be common to all fragments, otherwise equalizing the fragment chemical potentials has no meaning as their relative differences have no meaning.

As well as introducing PDFT, EBCW also included an illustration of PDFT, the purpose of which was to demonstrate that an exact PDFT calculation (i.e. if we had the exact functionals needed in Eq. (5)) does indeed yield that exact density and energy of the true system. In

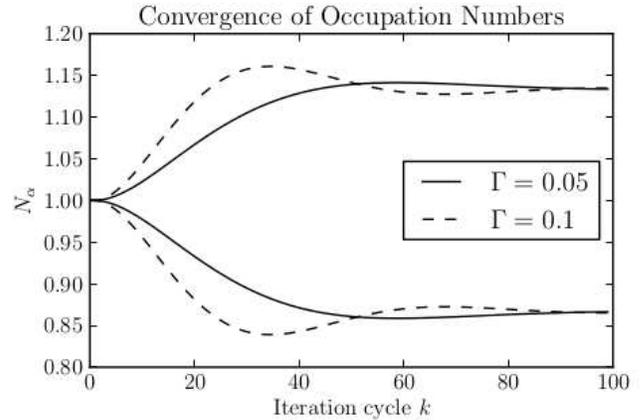


FIG. 1. The occupations of the 1-atom fragments for the 4-atom chain example of BM12 during the iteration cycle for two different values of Γ . Both calculations are initialized with the same fragment occupations, namely $N_i = 1$. Note that due to symmetry the two inner and two outer fragments in the chain will have the same occupations respectively.

reality, we do not have an explicit formula for the exact functional derivatives, but we may deduce the resulting potentials by performing additional calculations on the full system. Hence our demonstration comprised of non-interacting fermions in 1D where such calculations are computationally feasible. There are many methods for doing this inversion of a density[26–32], but in the end all should yield the same result. The discussion in BM about the performance and efficiency of the inversion scheme used in EBCW is entirely irrelevant to PDFT. We are not proposing this as a practical method; it was used only as part of a proof of principle calculation.

Substituting into Eq. (5), the definition of the KS potential, namely $v_s[n] = v[n] + v_{\text{HXC}}[n]$, we find

$$v_p^{(k+1)}(\mathbf{r}) = v_p^{(k)}(\mathbf{r}) + (v(\mathbf{r}) - v[n^{(k)}](\mathbf{r})) \quad (7)$$

as the equation for updating the partition potential during the iteration cycle where $v[n^{(k)}](\mathbf{r})$ is the external potential of an interacting system with density $n^{(k)}(\mathbf{r})$ (the sum of the fragment densities at iteration k). This is the equation actually used during the illustration of EBCW, guaranteeing the partition potential is global by working with it directly. This is similar to the later approach of Ref. 10. At each iteration cycle, it is simply added to each fragment potential $v_\alpha(\mathbf{r})$ to make the effective fragment potential. Of course $v[n^{(k)}](\mathbf{r})$ is an extremely complicated functional, so Eq. (7) is only useful for reference calculations like in EBCW. In practice, steps must be taken to ensure that $v_p(\mathbf{r})$ is global. For example, in Ref. 20, which uses the von Weizsäcker functional (VW), the partition potential is averaged over each fragment.

We now turn to the calculations in BM, which attempted to implement PDFT and test it on non-interacting systems similar to the illustration in EBCW.

However it is clear that they do not have a global partition potential, even discussing differences between the partition potential for each fragment. This can also be seen in figure 3 of BM, where the y-axis is labeled as $v_{p,1}(x)$. If they had reached the PDFFT solution (or even a solution for fixed occupations) the partition potential would be the same for each fragment and there would be no need to label their potentials 1, 2, etc. The results obtained in BM will not minimize Eq. (2) and so are not PDFFT calculations. Conclusions drawn from these calculations simply do not apply to PDFFT.

To set the fragment occupations *on-the-fly* using the algorithm discussed earlier, it is essential to have a global partition potential. As this is not the case in BM, the authors were led to wrongly conclude that the fragment occupations depend on the choice of parameter Γ and therefore are not unique. When implemented correctly, there is no dependence of the final fragment occupations on the parameter Γ . In Fig. 1, we use the same model used in BM and show the convergence of the fragment occupations for different choices of Γ . Although the individual curves for each choice are different and the rate of convergence for each is different, all converge to the same value.

We can also understand why the 'shifted VW' calculations in BM reproduce the PDFFT results, as in this calculation the partition potential they find will be global. This shift is regarded as an unphysical new constraint by BM, but it is in fact necessary to satisfy an already existing aspect of PDFFT.

Throughout BM, the von Weizsäcker kinetic energy functional is used for the fragment calculations. As is well-known, the VW functional is only exact for $N \leq 2$ electrons, but becomes inaccurate for larger values. Following Eq. (5) of BM, they attempt to perform a PDFFT calculation with fragments containing greater than 2 electrons. It is no surprise they cannot converge this calcula-

tion as they are incorrectly still using the VW functional for this case. This example in no way demonstrates any flaw with PDFFT. It merely reflects the flawed implementation and the authors preference for integer occupations. Indeed, the correct PDFFT occupations for their example are the not-quite-integers 1.962 and 2.038, for the two outer and inner wells, respectively.

Furthermore, contrary to what is claimed in BM, the central result of EBCW was not "convergence of the sum of the fragment densities to the exact total density". The main result of EBCW is that PDFFT will converge to the unique set of fragment densities given by Partition Theory. It was not our intention to imply that PDFFT is the only valid fragmentation scheme; the approaches of SCAD[6], self-consistent Hirshfeld[7, 8], Cortona[3], freeze-thaw[4], and the many other embedding schemes available[5, 9, 10, 12], may also reproduce the exact energy and density. There is, in principle, an infinite number of ways to divide up a density between fragments. PDFFT is merely one approach to this problem and one, we believe, which has some favorable properties. Work is ongoing into the behavior of PDFFT. For example, one particularly interesting aspect is the dependence of E_f on the fragment occupations, where, although PDFFT in general yields non-integer occupations, in certain situations integer occupations are favored[23].

Finally we also note that the calculations in BM and EBCW are both on non-interacting systems, where the differences between the various schemes mentioned above will typically be small.

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