

Comment on “Ability of nonperturbative density-functional theories to stabilize arbitrary solids”

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(Received 11 August 1994)

Kyrlidis and Brown [Phys. Rev. A **44**, 8141 (1991)] assert that the modified weighted density approximation of Denton and Ashcroft [Phys. Rev. A **39**, 4701 (1989)] may possess *two* solutions for the effective density. We show here that it has either one well-defined solution or none, the latter when the physical structure that is attempting to be mapped into an effective liquid does not exist. The absence of a solution when none is expected physically cannot, therefore, be characterized as a defect of the theory.

PACS number(s): 61.20.Gy, 64.70.Dv, 64.60.Cn

In a paper written about four years ago [1], Kyrlidis and Brown made a comparison between two density-functional theories, one the modified weighted density approximation [2] (MWDA) of Denton and Ashcroft and the other the generalized effective liquid approximation [3] of Lutsko and Baus. Their paper was motivated by an aim to stabilize crystalline silicon utilizing a Stillinger-Weber (SW) potential, an essential component of which is the presence of *three-body interactions* reflecting the covalent nature of the bonding characteristic of silicon. The authors observed that actual use of the SW potential would have made the computational effort very demanding and they resorted instead to a hard-sphere potential that among others of its properties, is of a purely *two-body* nature. On the basis of analysis with these purely two-body interactions, it was subsequently stated that within the chosen diamond structure some shortcomings of weighted density approximations could then be revealed.

It is well known, of course, that a diamond structure cannot be stabilized without the presence of three-body interactions, let alone with the hard-sphere potential, which favors close-packed structures (and even then only when the packing fraction exceeds 0.49). The authors reported that their aim was to study the effects of the chosen crystal lattice on the ensuing form of the weighted density. However, the latter is not determined by the (candidate) crystal structure *alone*; it is also determined in part by the assumed interaction between particles, which directly establishes the direct correlation function of the uniform liquid and its excess free energy per particle, both being essential ingredients of the MWDA. For a candidate diamond structure, the assumption of a hard-sphere potential for the interparticle interaction, even as a *reference*, is not a physically meaningful choice since it lacks certain essential features necessary to stabilize the particular lattice. Consequently, it is at once questionable whether the approach described above can be used as a test of *any* density-functional theory at all. Further, even within the framework of their announced goals, the authors made some statements that appear to reveal a serious misunderstanding of the physical nature

of the MWDA. In particular, they asserted repeatedly that the MWDA can possess *two solutions* for the weighted densities. These assertions seem to be based on an interpretation that the MWDA amounts *solely* to the solution of Eq. (11) of their paper, namely,

$$\hat{\rho} - \rho_s \left[1 - \frac{1}{4\beta f'_0(\hat{\rho})} \sum_{\mathbf{k} \neq 0} e^{-k^2/2\alpha} c_0^{(2)}(\mathbf{k}; \hat{\rho}) \times [1 + \cos(\mathbf{k} \cdot \mathbf{t})] \right] = 0 \quad (1)$$

[here c_0 is the direct correlation function of the homogeneous system and $f_0(\rho)$ the corresponding free energy per particle.] This is simply not the case: a further and quite essential ingredient of the MWDA is the constraint

$$\lim_{\rho(\mathbf{r}) \rightarrow \bar{\rho}} \hat{\rho}[\rho(\mathbf{r})] = \bar{\rho} \quad (2)$$

for any uniform density $\bar{\rho}$, a relation that is fundamental and one that is required by the normalization condition

$$\int d\mathbf{r} w(\mathbf{r}; \hat{\rho}) = 1. \quad (3)$$

As we show below, a proper recognition of the constraint (2) leads immediately to a unique identification of the solution of Eq. (1). The second “branch” shown in Fig. 1(b) of Ref. [1] is therefore *not* a MWDA solution because it does not satisfy the requirement (2) above and we believe it has been wrongly characterized as such by the authors.

From a quantitative point of view, an even more curious characteristic of what is termed “second solution” is its limiting behavior for small α . Insufficient data points in Fig. 1(b) are provided for a rigorous analysis, but the data point for the *smallest* value of $\alpha\sigma^2$ corresponds to a weighted density $\hat{\rho}\sigma^3 \approx 1.9$, i.e., to a hard-sphere liquid with a packing fraction $\hat{\eta} = (\pi/6)\hat{\rho}\sigma^3 \approx 1$. It is quite obvious that the packing fraction of the hard-sphere system can never exceed the value $\pi/\sqrt{18} = 0.74$ and even this is a value appropriate to a fcc *solid*, not to a liquid. The Percus-Yevick solution for $c_0^{(2)}$ and the associated $f_0(\hat{\rho})$ break down long before the packing fraction reaches the

apparent value unity, the *physical* attainment of which is an impossibility since space cannot be completely filled with nonoverlapping spheres. These quantities can only be used within the density limits for which they are established to be physically meaningful, which restricts the density to values below the close-packing limit.

It is also straightforward to show that the value $\hat{\eta}=1$ cannot be a solution of the MWDA iteration for any nonzero value of the localization parameter $\alpha\sigma^2$. To see this, consider Eq. (19) in Ref. [2], which is precisely the one solved by Kyrilidis and Brown for the fcc solid [to which the results of Fig. 1(b) refer], but now written in a slightly different form, namely,

$$\hat{\eta}(\eta_s, \alpha) = \eta_s \left[1 - \frac{3}{\pi\beta f'_0(\hat{\eta})} \sum_{\mathbf{G} \neq 0} e^{-G^2/2\alpha\hat{c}_0^{(2)}(\mathbf{G}, \hat{\eta})} \right], \quad (4)$$

where $\{\mathbf{G}\}$ is the set of reciprocal lattice vectors of the fcc lattice, $\eta_s = (\pi/6)\rho_s\sigma^3$, and $\hat{c}_0^{(2)} = c_0^{(2)}/\sigma^3$. From the Percus-Yevick solution for hard spheres, we can readily factor out the singular part of f'_0 and $\hat{c}_0^{(2)}$ at $\hat{\eta}=1$ to obtain

$$f'_0(\hat{\eta}) = \frac{1}{(1-\hat{\eta})^3} \phi(\hat{\eta}) \quad (5a)$$

and

$$\hat{c}_0^{(2)}(\mathbf{G}, \hat{\eta}) = \frac{1}{(1-\hat{\eta})^4} \psi(\mathbf{G}, \hat{\eta}), \quad (5b)$$

where both ϕ and ψ are by definition regular at $\hat{\eta}=1$. Substituting (5) into (4) we find

$$\hat{\eta}(\eta_s, \alpha) = \eta_s \left[1 - \frac{3}{\pi\beta\phi(\hat{\eta})(1-\hat{\eta})} \sum_{\mathbf{G} \neq 0} e^{-G^2/2\alpha\psi(\mathbf{G}, \hat{\eta})} \right]. \quad (6)$$

From Eq. (6) it is immediately clear that $\hat{\eta}=1$ can never be a solution for any nonzero value of α , no matter how small, simply because the right-hand side of Eq. (6) diverges, whereas the left-hand side remains finite. Though the "second branch" in Fig. 1(b) of Ref. [1] appears to approach exactly this limit, it is neither clear from the figure nor from the accompanying text what its detailed limiting behavior is. Might it, for example, break down as a solution at some small but nonvanishing

value of α ? Were this to be the case, then the limit $\alpha \rightarrow 0$ of this solution cannot exist, the conclusion then being that the information in Fig. 1(b) is actually incomplete as well as misleading. According to the general constraint (2), the nonexistence of a uniform density limit certainly rules as inadmissible the additionally proposed MWDA solution. We believe that clarification of this essential point is a significant omission on the part of the authors.

Finally, the authors take the MWDA to task, because for diamond structures and for high values of the localization parameter, they are evidently unable to find a mapping onto an effective liquid. As we point out above, for hard-sphere interactions alone the diamond solid is mechanically unstable, as is clear *a priori*. Thus, if for given pairwise interactions a structure does not exist, even in principle, and a proposed density functional approximation subsequently fails to map it into an effective liquid, should this then be considered a defect of the theory? If a "trial structure" is extremely unstable, i.e., it has a very high excess free energy relative to the thermodynamically correct state, there can be no physical reason to expect that an effective liquid that has the same high free-energy exists. The inability of the MWDA to locate a solution should therefore be seen as a correct manifestation of the extreme instability of the solid and not as a weakness of a particular version of density functional theory.

Our conclusion is therefore this: in contrast to the statements of the authors and in particular to the remarks about the MWDA made in the first paragraph of the summary of Ref. [1], the solution of the MWDA, when it exists, is always *unique* if proper account is taken of the boundary condition that it has to satisfy for small localizations. As far as we are aware there is as yet no demonstrated "pathology" in the MWDA, as the authors state in their summary. In view of this, we believe that at present their statement that the *non-MWDA*, unphysical "second solution" should affect the choice of the density-functional method used to minimize the free energy is simply untenable.

This work has been supported by the Alexander von Humboldt-Stiftung and the National Science Foundation through the Materials Science Center at Cornell University (Grant No. DMR-91-21654).

[1] Agathagelos Kyrilidis and Robert A. Brown, Phys. Rev. A **44**, 8141 (1991).

[2] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701

(1989).

[3] J. F. Lutsko and M. Baus, Phys. Rev. A **41**, 6647 (1990).