

Klüner *et al.* Reply: The preceding Comment [1] is concerned with whether we, in our Letter [2], adequately justified our hybrid wave function/density-functional (DFT) embedding theory and the choice of kinetic energy density functionals (KEDFs) used to construct the embedding operator v_{emb} . The Comment has two problems: (i) a misunderstanding of our theory and (ii) an example of questionable relevance.

First, length restrictions did not permit a complete re-derivation of the formalism; a thorough, formal justification is given *in detail* in [3,4]. The first criticism leveled is that since $T_s^{\text{nad}}[\rho_1, \rho_{11}]$ is a nonlinear functional of ρ_1 , use of v_{emb} as an operator must be postulated. This is simply not so. Our embedding potential, derived variationally within (formally exact) DFT as the operator that influences the density in the region of interest due to the presence of the surroundings, is the same as the one written by Wesolowski in his Eq. (1). Our v_{emb} is used *only* as an additional one-electron potential in the Fock operator to obtain the wave function in the embedded region, but *never* to obtain the total energy E_{tot} ; i.e., our E_{tot} does *not* contain $\langle \phi_i | (\delta T_s^{\text{nad}}[\rho_1, \rho_{11}] / \delta \rho_1) | \phi_i \rangle$, and hence we do not need to postulate its use and its nonlinearity is not an issue. To clarify, our E_{tot} is calculated as given in Eq. (16) of [4], where the subsystem interaction terms in E_{tot} appear only within the entire system's DFT total energy, $E_{\text{tot}}^{\text{DFT}}[\rho_{\text{tot}}]$. The embedded region total energies in Eq. (16), $E_I^{\text{ab,DFT}}$, involve only terms within that region; i.e., v_{emb} does not appear explicitly (to avoid double counting interactions). v_{emb} does, however, have an implicit effect on $E_I^{\text{ab,DFT}}$, as the wave functions in region I are affected by v_{emb} .

Wesolowski's second concern is the choice of KEDF and its corresponding potential. As stated in [2], details on the construction of the KEDF potential (KEFP)—again we do not use the KEDF itself, only its potential—are published elsewhere [5]. In the Letter we provided a number of tests for the validity and justification of the choice of KEFP: (i) a DFT in DFT embedding, in which the electron density was virtually identical to that of a periodic DFT calculation (verifying the accuracy of the KEFP and the embedding scheme; see Fig. 1) and (ii) the sensitivity of adsorption energies to the choice of KEFP was reported in Table II, Ref. [2]. These latter tests show the importance of including gradient corrections in both the exchange-correlation and KEFP to achieve high accuracy.

As evidence disputing the validity of our KEDF choice, Wesolowski offers references and the Comment's figure, all of which assess the ability of various KEDFs to describe weak intermolecular forces (e.g., dispersion). Surely it is clear that KEDFs appropriate for van der Waals interactions are not necessarily the ones appropriate for metals (the territory of our "claim"); it is well known that in the case of exchange-correlation functionals, those that work well for metals fall short in their description of weakly interacting molecules (the purview of Wesolowski's cases) [6]. We proved in our Letter that our choice of KEDF

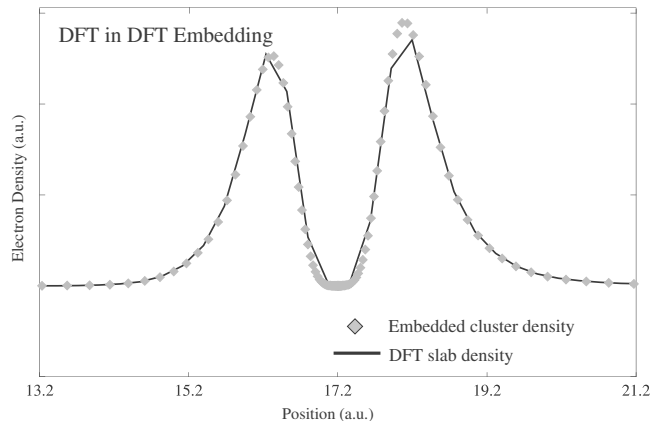


FIG. 1. DFT [local density approximation (LDA)] in DFT (LDA) embedding calculation for a Pd_3 cluster embedded in a three-layer Pd slab.

works properly for metals and whether it works for van der Waals or hydrogen-bonded systems was not claimed by us. (N.B., we did not apply the conventional gradient expansion up to second order as implied by Wesolowski; rather, we introduced a local truncation criterion based on the ratio of the Thomas-Fermi and von Weizsäcker potentials [5]; he does not provide in his papers or this figure results for such a functional.) Last, note that the Comment's figure showing the inaccuracy of the conventional gradient expansion for a molecular dimer is not relevant to our method, since, as explained above, we do not use the KEDF to calculate total energies as he did to generate the Comment's figure; we use only the kinetic energy *potential* in the embedding potential as an additive term to the Fock matrix. This is a second order effect and thus so are the approximations introduced. Therefore, the accuracy of the KEDFs used in our theory is not at all as crucial as in his orbital-free DFT method, where he must use it to obtain a total energy.

This work is supported by the NSF, the ARO, the AFOSR, and the DFG.

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Received 15 August 2001; published 3 May 2002
DOI: 10.1103/PhysRevLett.88.209702
PACS numbers: 71.15.-m, 73.20.Hb

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Comment on “Prediction of Electronic Excited States of Adsorbates on Metal Surfaces from First Principles”

In a recent Letter, Klüner *et al.* [1] reported a study of excited states of CO adsorbed on the Pd(111) surface using the embedded-molecule approach. Klüner *et al.* applied an *ad hoc* combination of two approaches (a) the wave-function formalism to describe the adsorbant and (b) the orbital-free first-principles-based embedding method introduced by Wesolowski and Warshel [2] which was based on Cortona’s formulation of density functional theory [3]. Some issues which might influence the obtained results were, however, not addressed in Ref. [1].

One is more general and concerns the idea of using $V_{\text{emb}}^{\text{eff}}$ of Ref. [2] as an “embedding operator.” $V_{\text{emb}}^{\text{eff}}$ was derived based on the variational principle and the representation of the ground-state Kohn-Sham total energy functional as a bifunctional $E[\rho_I, \rho_{II}]$. In Ref. [2], it was shown that embedding potentials appearing in various embedding approaches can be cast in a universal orbital-free kinetic-energy-dependent form obtained by means of constrained minimization of $E[\rho_I, \rho_{II}]$ in which only the electron density of the selected subsystem (ρ_I) is varied. Subtracting from the total effective potential defined in Eqs. (18)–(21) of Ref. [2] the component which corresponds to the isolated subsystem I leads to the following form of $V_{\text{emb}}^{\text{eff}}$:

$$V_{\text{emb}}^{\text{eff}} = \sum_{A_{II}} -\frac{Z_{A_{II}}}{|\mathbf{r} - \mathbf{R}_{A_{II}}|} + \int \frac{\rho_{II}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho_I(\mathbf{r}) + \rho_{II}(\mathbf{r})]}{\delta \rho_I} - \frac{\delta E_{xc}[\rho_I(\mathbf{r})]}{\delta \rho_I} + \frac{\delta T_s^{\text{nad}}[\rho_I, \rho_{II}]}{\delta \rho_I}, \quad (1)$$

where $T_s^{\text{nad}}[\rho_I, \rho_{II}] = T_s[\rho_I + \rho_{II}] - T_s[\rho_I] - T_s[\rho_{II}]$. This form of $V_{\text{emb}}^{\text{eff}}$ is a result of a decomposition of the total effective potential in ground-state density-functional theory. Since $T_s^{\text{nad}}[\rho_I, \rho_{II}]$ is not a linear functional of ρ_I , the use of Eq. (1) as an “embedding operator” should be clearly identified as a postulate.

The second issue concerns the choice for the approximate kinetic energy functional in Ref. [1]. In the embedding formalism introduced in Ref. [2], an approximate kinetic energy functional (\tilde{T}_s) appears always in expressions involving differences of T_s . The accuracy of $\tilde{T}_s^{\text{nad}}[\rho_I, \rho_{II}]$ appears, therefore, as a crucial ingredient of this embedding scheme, *not* the absolute accuracy of its individual components: $\tilde{T}_s[\rho_I + \rho_{II}]$, $\tilde{T}_s[\rho_I]$, or $\tilde{T}_s[\rho_{II}]$. Our direct analyses of the accuracy of different approximations for $\tilde{T}_s^{\text{nad}}[\rho_I, \rho_{II}]$ [4] showed that the accuracy of \tilde{T}_s does not necessarily imply a good accuracy of $\tilde{T}_s^{\text{nad}}[\rho_I, \rho_{II}]$. In fact, the second-order expansion leads to a much worse approximation for $T_s^{\text{nad}}[\rho_I, \rho_{II}]$ (see Fig. 1) and for $\frac{\delta T_s^{\text{nad}}[\rho_I, \rho_{II}]}{\delta \rho_I}$ (see Fig. 3b in Ref. [4a]) than does the Thomas-Fermi model. The authors of Ref. [1] appear to

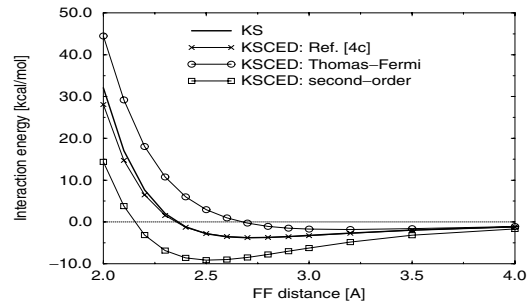


FIG. 1. The potential energy curve for the FH...FH dimer obtained using Kohn-Sham calculations (KS) and the subsystem based approach (KSCED) using different approximate expressions for $T_s^{\text{nad}}[\rho_I, \rho_{II}]$. See Ref. [4c] for details.

have overlooked this particular feature of $T_s^{\text{nad}}[\rho_I, \rho_{II}]$ (and $\frac{\delta T_s^{\text{nad}}[\rho_I, \rho_{II}]}{\delta \rho_I}$) and rely on a rather good performance of their approximation for $\frac{\delta \tilde{T}_s[\rho]}{\delta \rho}$ without verifying the accuracy of $\frac{\delta \tilde{T}_s[\rho_I + \rho_{II}]}{\delta \rho_I} - \frac{\delta \tilde{T}_s[\rho_I]}{\delta \rho_I}$. We performed such studies [4] leading to a very good approximation for $\frac{\delta T_s^{\text{nad}}[\rho_I, \rho_{II}]}{\delta \rho_I}$ for small $\rho_I - \rho_{II}$ overlaps. It has been applied for various problems (see Ref. [5] and references therein).

We strongly feel that the above issues should have been clarified by the authors prior to claiming, as they do, far-reaching applicability of the method they devise. Strong dependence of the interaction energies collected in Table II of Ref. [1] on the choice of the approximation for $T_s[\rho]$ indicates the need of dedicated studies of the accuracy of $\frac{\delta \tilde{T}_s^{\text{nad}}[\rho_I, \rho_{II}]}{\delta \rho_I}$ applied in Ref. [1]. Moreover, the applied approximation for $T_s[\rho]$ [see Eq. (5) in Ref. [1]] seems to be very similar to the conventional second-order expansion—a rather poor approximation for $\frac{\delta T_s^{\text{nad}}[\rho_I, \rho_{II}]}{\delta \rho_I}$. Therefore, the good numerical results obtained in Ref. [1] for a particular problem cannot be used as a validation for general accuracy of the applied embedding potential.

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Received 6 July 2001; published 3 May 2002

DOI: 10.1103/PhysRevLett.88.209701

PACS numbers: 71.15.-m, 73.20.Hb

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