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van der Waals bonds in density-functional theory

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The concept of implicit exchange-correlation energy functionals [optimized potential method (OPM)] is applied to the helium and neon dimers. Using the lowest order correlation functional obtained within Kohn-Sham perturbation theory we find energy surfaces in reasonable quantitative agreement with the exact results, thus demonstrating that the OPM allows a seamless description of van der Waals bond systems.

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Since the seminal paper of Zaremba and Kohn [1] the description of van der Waals (vdW) bonds has been a major topic in density functional theory (DFT) [2–9]. The interest stems from the fact that the current standard approximations for the exchange-correlation (xc) energy functional E_{xc}, the local density (LDA), and generalized gradient (GGA) approximations, do not reproduce long-range forces which extend into regions of space with vanishing density. For some time, research in DFT has thus focused on the prediction of the leading vdW coefficient C_6 which is accessible via the polarizabilities obtained from the Kohn-Sham (KS) orbitals of the isolated systems (atoms, molecular components) [3–7,9].

However, for actual applications a seamless DFT description of vdW forces is required, i.e., a xc functional which not only reproduces the asymptotic $1/R^6$ limit but rather the complete energy surface $E_b(R)$ (with R denoting the internuclear separation) of vdW bond systems (and, simultaneously, covalent bonds, etc). This fact is emphasized by the observation that the $1/R^6$ attraction is not the only binding mechanism in these systems: in spite of their failure in the large-R regime, GGAs have been shown [10] to provide more realistic results for noble gas dimers than the LDA, reflecting the small, but nonnegligible density overlap at the equilibrium separation R_e (for He_2 one finds a density overlap of roughly 1% of the density at the r-expectation value of atomic Helium).

Recently, three suggestions for a seamless DFT treatment of vdW systems have been put forward [6–8], all three relying on the adiabatic connection formula for E_{xc} together with some approximation for its crucial ingredient, the coupling-constant-dependent response function. However, while these schemes yield rather accurate values for C_6, full scale applications to vdW-bond molecules are not yet available.

A systematic (i.e., universal and parameter-free) and directly applicable approach to a seamless DFT description is offered by the concept of implicit, i.e., orbital-dependent, xc functionals for which the corresponding xc potential has to be evaluated via the optimized potential method (OPM) [11]. In most applications of the OPM [12–14] the exact representation of the exchange energy E_{x} via the Fock term (evaluated with the KS orbitals ϕ_k) is combined with a conventional density functional for the correlation energy E_{c}. However, recently an orbital-dependent correlation functional has been introduced on the basis of KS perturbation theory [15]. This functional consists of two contributions, the first one having the same form as the second order Møller-Plesset expression (MP2) and the second one reflecting the difference between the exchange-only (x only) OPM and the Hartree-Fock (HF) ground state energy (ΔHF)

$$E_{\mathrm{c}}^{(2)}=E_{\mathrm{c}}^{\mathrm{MP2}}+E_{\mathrm{c}}^{\Delta\mathrm{HF}}, \tag{1}$$

$$E_{\mathrm{c}}^{\mathrm{MP2}}=\frac{e^4}{2}\sum_{\epsilon_i,\epsilon_j\leqslant\epsilon_F<\epsilon_k,\epsilon_l}\frac{(ij||kl)[(ij||kl)-(ij||lk)]}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l}, \tag{2}$$

$$E_{\mathrm{c}}^{\Delta\mathrm{HF}}=\sum_{\epsilon_i\leqslant\epsilon_F<\epsilon_l}\frac{1}{\epsilon_i-\epsilon_l}\;\Big|\langle i|v_x|l\rangle+e^2\sum_{\epsilon_j\leqslant\epsilon_F}(ij||jl)\Big|^2, \tag{3}$$

$$(ij||kl)=\int d^3r_1\int d^3r_2\;\frac{\phi_i^\dagger(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_1)\phi_j^\dagger(\boldsymbol{r}_2)\phi_l(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}, \tag{4}$$

where $\langle i|v_x|l\rangle=\int d^3r\;\phi_i^\dagger(\boldsymbol{r})\phi_l(\boldsymbol{r})v_x(\boldsymbol{r})$, ϵ_F is the Fermi level and v_x the OPM exchange potential. It has been shown that $E_c^{(2)}$ approaches the asymptotic vdW limit [16] and yields C_6 coefficients in reasonable quantitative agreement with experimental values for light atoms [7,9], notwithstanding its perturbative character (at least, as long as the atomic ϕ_i result from an OPM type v_x). In the present study we apply the combination of the exact E_{x} and $E_{\mathrm{c}}^{(2)}$ to He_2 and Ne_2, in order to explicitly demonstrate that this functional (called FC2 hereafter) does in fact reproduce the complete nature of vdW bonds.

For the solution of the two-center Kohn-Sham equations we use prolate spheroidal coordinates ξ,η,φ,

$$\xi=\frac{r_1+r_2}{R},\quad 1\leqslant\xi<\infty, \tag{5}$$

$$\eta=\frac{r_1-r_2}{R},\quad -1\leqslant\eta\leqslant1, \tag{6}$$

$$\varphi=\tan\left(\frac{y}{x}\right),\quad 0\leqslant\varphi\leqslant2\pi, \tag{7}$$

where r_1, r_2 are the distances between the electronic coordinate $\boldsymbol{r}$ and the two nuclei at the positions $(0,0,\pm R/2)$, $r_{1,2}=[x^2+y^2+(z\pm R/2)^2]^{1/2}$. Due to the rotational symmetry with respect to the internuclear axis the KS orbitals can be classified by the angular momentum projection quantum number m,

$$\phi_i(\boldsymbol{r}) = \psi_{k,|m|}(\xi,\eta) e^{im\varphi} \chi_\sigma , \tag{8}$$

with $m=0,\pm 1,\pm 2,\ldots,\ k=1,2,\ldots,$ and χ_σ denoting the standard Pauli spinors. The cylindrical KS orbitals $\psi_{k,|m|}(\xi,\eta)$ are then expanded in terms of a nonorthogonal Hylleraas basis

$$\psi_{k,|m|}(\xi,\eta) = \sum_{n=0}^{n_{\max}} \sum_{l=|m|}^{l_{\max}+|m|} c^k_{nl|m|} P_l^{|m|}(\eta)(\xi^2-1)^{|m|/2} \times \exp\left(-\frac{\xi-1}{2a}\right) L_n^{|m|}\left(\frac{\xi-1}{a}\right), \tag{9}$$

where the L_n^m and P_l^m are generalized Laguerre polynomials and associated Legendre functions, respectively, and a is an adjustable parameter. The resulting selfconsistent algebraic eigenvalue problem has been discussed in detail in Ref. [17] to which we refer the reader for further information.

For the evaluation of the Slater integrals in both the exact E_x and the correlation functional (1) a multipole expansion of the Coulomb interaction [18] has been used,

$$\begin{aligned}(ij||kl) = {} & (2\pi)^2 \left(\frac{R}{2}\right)^5 \delta_{\sigma_i,\sigma_k} \delta_{\sigma_j,\sigma_l} \delta_{m_i+m_j,m_k+m_l} (-1)^M \\ & \times \sum_{L=M}^{\infty} (2L+1) \left[\frac{(L-M)!}{(L+M)!}\right]^2 \int_1^\infty d\xi_1 \int_1^\infty d\xi_2 \\ & \times \{\xi_1^2 f_{ik}^L(\xi_1) - g_{ik}^L(\xi_1)\} \{\xi_2^2 f_{jl}^L(\xi_2) - g_{jl}^L(\xi_2)\} \\ & \times \{\Theta(\xi_1-\xi_2) Q_L^M(\xi_1) P_L^M(\xi_2) \\ & + \Theta(\xi_2-\xi_1) P_L^M(\xi_1) Q_L^M(\xi_2)\}\end{aligned} \tag{10}$$

with $M=|m_i-m_k|=|m_j-m_l|$,

$$f_{ij}^L(\xi) = \int_{-1}^{1} d\eta\, P_L^{|m_i-m_j|}(\eta) \psi_{k_i|m_i|}(\xi,\eta) \psi_{k_j|m_j|}(\xi,\eta),$$

$$g_{ij}^L(\xi) = \int_{-1}^{1} d\eta\, \eta^2 P_L^{|m_i-m_j|}(\eta) \psi_{k_i|m_i|}(\xi,\eta) \psi_{k_j|m_j|}(\xi,\eta),$$

and Q_L^M denoting the associated Legendre functions of second kind. A multipole expansion has also been utilized for the evaluation of the Hartree potential

$$v_H(\xi,\eta) = \frac{1}{2} \sum_{l=0}^{\infty} (2l+1) \zeta_l(\xi) P_l(\eta). \tag{11}$$

In contrast to the Slater integrals (10), the ζ_l have not been calculated by direct integration, but rather by solution of the corresponding differential equations via a shooting procedure (for details see Ref. [17]), which results in much more accurate Hartree potentials and energies E_H.

TABLE I. N_ξ and $l_{\max}$ together with corresponding errors δ for the individual components of $E_b(R)$ (all δ in μHartree, $R=10$ Bohr for He$_2$, $R=7$ Bohr for Ne$_2$). The $N_\xi, l_{\max}$ values from which the δ are extracted are given in parentheses.

		$E_b^{\text{x-only}}$	Δ^{MP2}	$\Delta^{\Delta\text{HF}}$
He$_2$	N_ξ	512: $\delta=0.1$ (512 vs 128)	128: $\delta=0.1$ (128 vs 64)	512: $\delta=0.0$ (512 vs 128)
	$l_{\max}$	23: $\delta=0.0$ (23 vs 20)	27: $\delta=0.4$ (27 vs 23)	23: $\delta=0.0$ (23 vs 20)
Ne$_2$	N_ξ	512: $\delta=0.7$ (512 vs 128)	64: $\delta=0.3$ (64 vs 32)	128: $\delta=0.1$ (128 vs 64)
	$l_{\max}$	33: $\delta=16.6$ (33 vs 29)	27: $\delta=3.9$ (27 vs 23)	29: $\delta=0.1$ (29 vs 23)

The numerical solution of the OPM integral equation is a rather time-consuming procedure for E_x (compare Refs. [12,14,19,20]) and has not yet been successfully implemented for the functional (1). We have thus used the Krieger-Li-Iafrate approximation [19] for the calculation of v_x which has been shown to give very accurate results for a number of systems, in particular for light atoms (see, e.g., Ref. [19]). $E_c^{(2)}$, on the other hand, has been evaluated perturbatively which should be legitimate in view of the fact that for finite systems the correlation potential is only a minor component of the total KS potential.

In our calculations the basis parameter a has been chosen so that the position r_1+r_2 of the outermost node of the highest Laguerre polynomial $L_n^{|m|}((\xi-1)/a)$ in the basis remains invariant when R varies. This essentially leads to a proportionality of a with $1/R$. For both E_{xc} and E_H the multipole expansion has been truncated at the highest angular momentum available in the basis $l_{\max}$ (see Table I). This is consistent with the fact that the multipole expansion of the density is determined via Eq. (8) only up to $l=l_{\max}$. Further increase of the highest multipoles in Eqs. (10) and (11) did not lead to any significant changes in the relevant energies.

All numerical integrations were performed via Gauss-Legendre quadrature. In the case of the Slater integrals this implies an integration over a continuous, but nondifferentiable function of ξ [due to the step functions in Eq. (10)] with an integration formula designed for polynomials. While all other quantities (such as external energies or E_H) are rapidly converging with increasing size N_ξ of the ξ grid, the accurate calculation of Eq. (10) requires rather large ξ meshes (in order to reduce the error introduced in the vicinity of $\xi_1=\xi_2$ — this error scales quadratically with $1/N_\xi$). Fortunately, the absolute magnitude of $E_c^{(2)}$ is much smaller than that of E_x, so that a larger relative error can be tolerated in $E_c^{(2)}$ than in E_x. In order to obtain the total energy as accurately as possible different spatial grids have been applied for the self-consistent calculation of the x-only ground state energy $E_{\text{tot}}^{\text{x-only}}$ and the perturbative evaluation of $E_c^{(2)}$. On the other hand, all integrands are essentially polynomial with respect to η, so that one roughly needs $3l_{\max}/2$ η-mesh points to deal with a basis of size $l_{\max}$ [for this basis the crucial product of density times potential contains $P_{l_{\max}}^m(\eta)^3$ as highest order polynomial]. We have explicitly verified that all our results are converged to about 0.1 μHartree with respect to the number of η-mesh points.

For the evaluation of the energy surface,

$$E_b(R)=E_{\rm tot}[{\rm X}_2](R)-2E_{\rm tot}[{\rm X}](R), \tag{12}$$

the atomic ground state energy $E_{\rm tot}[{\rm X}](R)$ has been calculated with the two-center code with one atom at the position $(0,0,R/2)$ and the second center remaining empty. Using identical basis parameter, basis size, and grid, this procedure has the advantage that most of the error due to basis set truncation and of the error introduced by the ξ integration cancels out between the atomic and the molecular energies: the energy surface is much more insensitive to numerical limitations than the individual energies (as illustrated in Table I—see below).

For He_2 a basis with $n_{\rm max}=14$ has been used throughout. The more critical parameters N_ξ and $l_{\rm max}$ are given in Table I. For instance, for He_2 the x-only energy has been evaluated with $N_\xi=512$ and $l_{\rm max}=23$. The quality of this basis and grid can be checked by comparison of the result for a single helium atom at position $(0,0,R/2)$ with the result of a highly accurate spherical calculation [20]. Even for the largest R considered (10 Bohr) the $E_{\rm tot}^{\text{x-only}}$ obtained with the two-center code differs from that of the one-center calculation by only 3.5 μHartree. Moreover, in the range 4 Bohr$\leqslant R\leqslant$10 Bohr the atomic $E_{\rm tot}^{\text{x-only}}$ varies by less than 0.1 μHartree, which demonstrates both the adequate choice of the basis parameter a and the convergence with respect to $l_{\rm max}$.

Nevertheless, compared with the total well depth of the (essentially) exact variational $E_b(R)$ of 34.7 μHartree [21] an error of 3.5 μHartree would not be really satisfying. Fortunately, the final criterion for convergence is the variation of $E_b(R)$ when the grid or basis sizes are varied. In Table I we also list the changes in the individual components of $E_b(R)$, i.e., $E_b^{\text{x-only}}(R)$ and

$$\Delta^{\rm MP2}(R)=E_c^{\rm MP2}[{\rm X}_2](R)-2E_c^{\rm MP2}[{\rm X}](R), \tag{13}$$

$$\Delta^{\Delta{\rm HF}}(R)=E_c^{\Delta{\rm HF}}[{\rm X}_2](R)-2E_c^{\Delta{\rm HF}}[{\rm X}](R), \tag{14}$$

resulting from a reduction of either N_ξ or $l_{\rm max}$ (the corresponding values are also given in Table I). In the case of $l_{\rm max}$ the errors in Table I correspond to the largest and thus most critical R values. For the perturbative evaluation of $E_c^{(2)}$ all excitations into KS states with $m=0,\pm1,\pm2$ have been taken into account. The importance of excitations into states with $m=\pm3$ has been checked for $R=8$ Bohr: their contribution to $E_b(R)$ is only 0.1 μHartree. Taking all information together our final $E_b(R)$ for He_2 is accurate within less than 1 μHartree.

This accuracy is confirmed by the value for C_6 which is extracted from our numerical $E_b(R)$ under the assumption that for $R=10$ Bohr $E_b(R)\equiv -C_6/R^6$: we find $C_6=2.26$ Hartree Bohr^6, which deviates by only 36% from the value of 1.66 Hartree Bohr^6 obtained via the atomic KS polarizability of helium [7,9], corresponding to an absolute error of 0.6 μHartree.

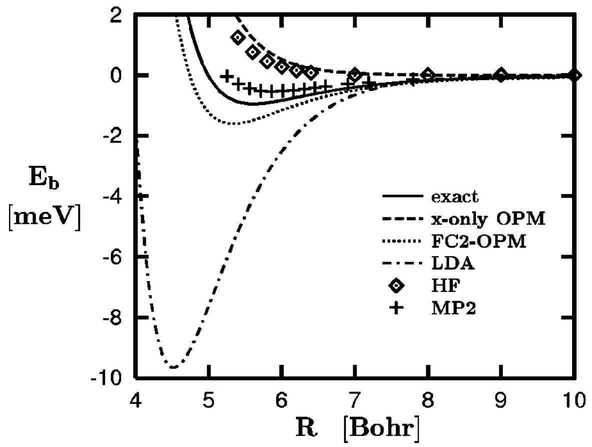

FIG. 1. Energy surface of He_2: x-only and correlated OPM data versus LDA, HF [22], MP2 [23], and exact [21] results.

The values of N_ξ and $l_{\rm max}$ used for Ne_2 are also given in Table I (again $n_{\rm max}=14$). The reduced grid employed for $E_c^{\rm MP2}$ reflects the high computational cost of the large number of pairs of occupied orbitals present in Ne_2. For the same reason excitations of the $1s$ electrons have not been included in the calculation of $E_c^{\rm MP2}$ as their contributions cancel out in $E_b(R)$. For $E_c^{\rm MP2}$ all excitations into states with $m=0,\pm1,\pm2,\pm3$ have been taken into account. For $R=8$ Bohr the inclusion of unoccupied states with $m=\pm3$ affects $E_b(R)$ by 1.1μHartree, so that the neglect of higher m states seems legitimate. Taking everything together, we expect the numerical accuracy of the Ne-Ne energy surface to be better than 20 μHartree, with $l_{\rm max}$ being the limiting factor.

Our results for He_2 are summarized in Figs. 1,2. Figure 1 shows $E_b(R)$ for three DFT variants in comparison with HF [22], conventional MP2 [23] and variational results [21]. While the LDA does yield a bound Helium dimer, the equilibrium separation R_e is predicted too small by 1.1 Bohr and the corresponding well depth D_e is too large by an order of magnitude (all our LDA results are in close agreement with those of Ref. [10]). This reflects the general perception that

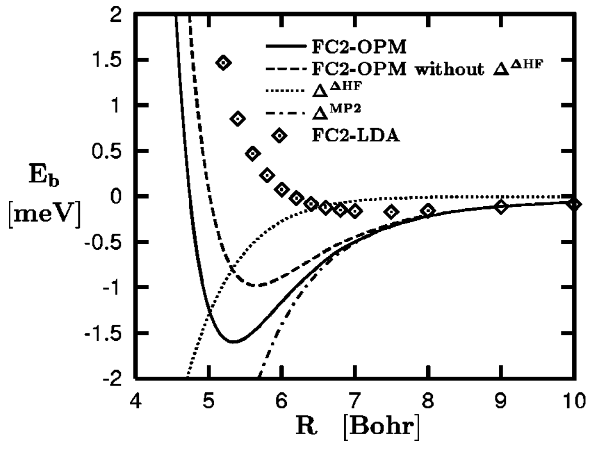

FIG. 2. Energy surface of He_2: decomposition of FC2- OPM result into x-only, ΔHF, and MP2 contributions. Also given is a perturbative FC2 result based on LDA orbitals.

the LDA is not suitable for describing vdW bonds. In consistency with the HF result, the x-only OPM produces a strictly repulsive $E_b(R)$. Inclusion of $E_c^{(2)}$ (abbreviated by FC2-OPM), on the other hand, leads to an energy surface which is about as close to the variational $E_b(R)$ as the MP2 data: the FC2-OPM underestimates R_e as much (0.2 Bohr) as the MP2 approach overestimates it. Accordingly, the FC2-OPM overestimates D_e by about 50%, while MP2 underestimates it by 35%. Clearly, higher order correlation corrections are required to obtain a complete quantitative agreement [23–25].

The role of the individual components of $E_c^{(2)}$ is analyzed in Fig. 2, where we have plotted $\Delta^{\Delta \mathrm{HF}}$ and Δ^{MP2}. While Δ^{MP2} dominates, $\Delta^{\Delta \mathrm{HF}}$ nevertheless is not negligible in the vicinity of R_e. This becomes particularly obvious if one compares the complete $E_b(R)$ with the energy surface obtained by neglect of $\Delta^{\Delta \mathrm{HF}}$ (see Fig. 2).

The observation that the well depth predicted by the OPM is larger than the HF result (and correspondingly R_e is smaller) can be traced back to the size of E_c^{MP2}, which, quite generally, is larger in the case of the OPM (see Ref. [26]). This reflects the fact that the gap between the highest occupied and the lowest unoccupied orbitals is smaller in the case of the x-only OPM ($\epsilon^{\mathrm{HOMO}} = -916$ mHartree, $\epsilon^{\mathrm{LUMO}} = -172$ mHartree at $R = 5.8$ Bohr) than for HF: as the x-only OPM and HF approaches give essentially identical ϵ^{HOMO}, the difference between the respective E_c^{MP2} is controlled by the size of the OPM's ϵ^{LUMO}, i.e., the lowest level of the complete Rydberg series which the OPM generates [11,16] (a more detailed analysis of the OPM spectrum will be given in Ref. [27]). As for He_2 the highest occupied level is rather strongly bound; the LUMO contribution does not reduce the gap too much and the OPM value for E_c^{MP2} is only about 20% larger than the HF result, similar to the case of atomic helium [26]. This difference is then transferred into Δ^{MP2}. Note, however, that even for H_2 for which the OPM gap is considerably smaller than for He_2 rather realistic spectroscopic parameters are found [26].

In Fig. 2 we have also plotted the energy surface obtained by a perturbative evaluation of the FC2 energy, using self-consistent LDA orbitals (FC2-LDA). In this case $E_c^{\Delta \mathrm{HF}}$ involves the difference between the nonlocal HF exchange and the LDA xc potential, and the Fock expression for E_x is also evaluated with LDA orbitals. The result of this procedure is rather different from that of the consistent OPM approach. This failure of the FC2-LDA originates from two sources. On the one hand, a significant error is introduced by the perturbative evaluation of the comparatively large E_x, although the correction (3) makes both the x-only OPM and the LDA-based ground state energies approach the HF value: at $R = 5.8$ Bohr the sum of the x-only OPM ground state energy and $E_c^{\Delta \mathrm{HF}}$ (evaluated with OPM orbitals) is 3.55 mHartree more attractive than its LDA-based counterpart. On the other hand, LDA orbitals and eigenvalues lead to a E_c^{MP2} which is 1.65 mHartree larger than that produced by the OPM states. This can be explained by the fact that the LDA gap is 20% smaller than the OPM value: while, for neutral systems, the LDA in general does not support any unoccupied bound states (similar to the HF), it substantially underestimates the eigenvalue of the highest occupied state ($\epsilon^{\mathrm{HOMO}} = -572$ mHartree, $\epsilon^{\mathrm{LUMO}} = +19$ mHartree for our basis), leading to a rather small net gap. Adding up both effects gives a net error of 1.90 mHartree, only part of which is cancelled by the subtraction of the corresponding atomic energies.

TABLE II. Bond length R_e, dissociation energy D_e (including zero-point energy) and harmonic frequency ω_e of Ne_2: FC2-OPM and LDA versus MP2 [23] and exact results [21].

	R_e (Bohr)	D_e (meV)	ω_e (cm^{-1})
LDA	4.97	20.3	80.0
FC2-OPM	5.48	8.3	45.7
MP2	6.06	2.3	23.1
Exact	5.84	3.6	28.4

Our results for Ne_2 are given in Table II. As for He_2 the LDA predicts a bound neon dimer, its R_e, however, being too small by 0.9 Bohr and its D_e being too large by a factor of 5. The spectroscopic constants obtained with the FC2-OPM, on the other hand, are much more realistic, their deviations from the exact values being roughly a factor of 2.5 smaller than those of the LDA. While the conventional MP2 results are even closer to the exact values than the FC2-OPM data, the Ne-Ne interaction potential is nevertheless reproduced semiquantitatively by the OPM scheme.

In summary, our results demonstrate that the FC2-OPM contains the basic physics required to reproduce vdW bonds. However, as in conventional many-body approaches, higher order correlation corrections have to be taken into account for a fully quantitative description of noble gas dimers (for state-of-the-art calculations beyond the MP2 level see Refs. [23–25]). One can nevertheless hope that for molecules in which dispersive forces do not completely dominate the molecular structure the inclusion of the essential features of the vdW interaction via the FC2 functional is sufficient. We have also analyzed the suitability of a fully perturbative evaluation of the FC2 functional on the basis of self-consistent LDA orbitals: while this approach reproduces the $1/R^6$-tail of $E_b(R)$ at least qualitatively, it completely fails in the actual bonding region. This demonstrates that functionals with the correct large-R behavior are not automatically suitable for applications to vdW bond systems and that the success of the FC2-OPM procedure is a nontrivial result.

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