

Comment on “Total Energy Method from Many-Body Formulation”

Recently, Aryasetiawan *et al.* [1] used a variational approach based on many-body perturbation theory (MBPT) [2] to calculate the total energy of H_2 at bond lengths $R \leq 4.5a_0$. The actual variational functional they chose [3] was evaluated at a noninteracting Green function, however, which makes their implementation strictly equivalent to the random phase approximation (RPA). In the context of density functional theory (DFT), recent studies on H_2 , Be_2 [4], and other molecules [5] show that the RPA may give rather accurate *differences* of total energies. Yet contrary to the findings of Ref. [1], *absolute* total energies are expected to be much too negative. We show this for H_2 , where we present full RPA binding and total energy curves, and question the results of Ref. [1].

In DFT, the RPA total energy may be evaluated as $E_{DFT}^{RPA}[n] = E^{LDA} - E_{xc}^{LDA} + E_{xc}^{RPA}$ which we note to be equivalent to the Letter’s Eq. (13). There the term $\Phi_x + \Phi_c^{RPA}$ is equivalent to the RPA exchange-correlation energy defined by $E_{xc}^{RPA}[n] = E_x + \int_0^1 d\lambda \text{tr}\{v(P_\lambda^{RPA} - P_0)\}$, the fluctuation-dissipation theorem averaged over the coupling strength λ . For densities and orbitals obtained in the local-density approximation (LDA), the other terms are the same already. Now $E_x \equiv \Phi_x$ is the Kohn-Sham exchange energy, and for the RPA polarization, $P_\lambda^{RPA} = (1 - \lambda P_0 v)^{-1} P_0$, the λ integration yields the correlation energy $E_c^{RPA} \equiv \Phi_c^{RPA}$, identical to Eq. (6) of the Letter.

We have calculated the binding energy curve $\Delta E(R)$ for H_2 relative to two free H atoms, using the DFT/RPA method [4,6] and the total density of (spin-unrestricted) exact Kohn-Sham exchange, which itself is exact for $R \rightarrow \infty$. In Fig. 1 we plot this curve and the related absolute total energies, $E = \Delta E + 2E(H_{at})$. The RPA clearly gives an accurate atomization energy of 0.347 Ry, and the exact value is 0.349 Ry. Moreover, it dissociates H_2 properly into the free atoms, without the need for (symmetry breaking) spin orbitals as in L(S)DA

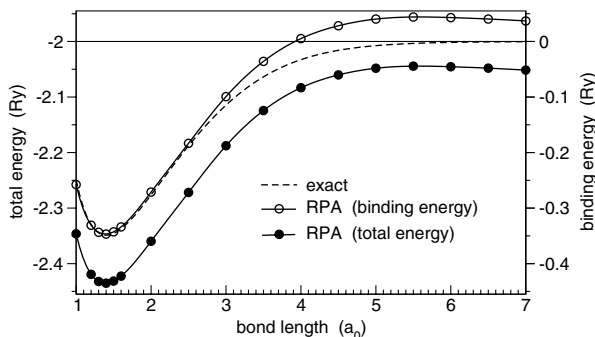


FIG. 1. Binding energies of H_2 (right scale), calculated in the RPA, closely approximate the exact values (from Ref. [10] of Ref. [1]), for bond lengths $R \leq 3a_0$. *Absolute* total energies (left scale) are markedly too negative in the RPA, for all R .

[7]. Yet the RPA total energies are too negative for any R , by up to -85 mRy at $R = 1.4a_0$, i.e., twice the (spurious self-) correlation energy of a H atom, -43 mRy. Similar errors are found in the He atom [4] and the uniform electron gas [8], and cancel only in total energy differences [9]. Our data are consistent with these findings, and do not change significantly when we use the LDA instead of exact exchange orbitals. By contrast, the RPA total energies in Fig. 1 of Ref. [1] are too high in energy, lying below the exact data by only ≈ 22 mRy for $R = 1.4a_0$ [10]. This might signal a lack of convergence, notably with respect to scattering states, in the calculation of Ref. [1]. Thus we conclude that the agreement of the RPA with the exact total energies as claimed in Ref. [1] is only apparent.

Our Fig. 1 also shows, unlike Ref. [1], that the RPA binding energy curve is too repulsive at intermediate $R \approx 5a_0$, while it is quite accurate at smaller or larger R . A similar behavior is observed for N_2 [5] and Be_2 . Yet perfection is not expected from the RPA; it is, e.g., not self-correlation free. We agree with Aryasetiawan *et al.* on the need for developing computationally viable total energy methods to go beyond today’s DFT. Exploring the concepts of both MBPT and DFT should be fruitful. Progress beyond the RPA is being achieved already, as Refs. [2,4,5,9,11] show.

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