Failure of the random-phase-approximation correlation energy

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The random phase approximation (RPA) is thought to be a successful method; however, basic errors have been found that have massive implications in the simplest molecular systems. The observed successes and failures are rationalized by examining its performance against exact conditions on the energy for fractional charges and fractional spins. Extremely simple tests reveal that the RPA method satisfies the constancy condition for fractional spins that leads to correct dissociation of closed-shell molecules and no static correlation error (such as in H_2 dissociation) but massively fails for dissociation of odd electron systems, with an enormous delocalization error (such as $H_2{}^+$ dissociation). Other methods related to the RPA, including the Hartree-Fock response (RPAE) or range-separated RPA, can reduce this delocalization error but only at the cost of increasing the static correlation error. None of the RPA methods have the discontinuous nature required to satisfy both exact conditions and the full unified condition (e.g., dissociation of $H_2{}^+$ and H_2 at the same time), emphasizing the need to go beyond differentiable energy functionals of the orbitals and eigenvalues.

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The random phase approximation (RPA) [1], formulated within the adiabatic-connection fluctuation dissipation theorem, provides an appealing definition of the exchange-correlation energy. It can also be simply viewed [2] from a density-functional-theory (DFT) perspective as a functional of all (occupied plus virtual) orbitals and eigenvalues in the Kohn-Sham (KS) formalism. There has been much recent attention given to the RPA method in molecules and solids [3–14], highlighted by the work of Furche [3,4], who has shown a practical way to calculate the correlation energy in the KS context in a similar fashion to the wave-function approach [15]. Much of the interest in the RPA method comes from the improved description of two key aspects for which many other density-functional approximations (DFAs) encounter severe problems: One is the description of the weak van der Waals interaction, as typified by molecules such as He_2 or Ne_2; the other is the description of static correlation, as seen in the stretching of H_2 [11] and N_2 [16]. Other efforts to include unoccupied orbitals into the exchange-correlation energy, such as the second-order Möller-Pleset (MP2) or second-order Görling-Levy (GL2) methods, have not been so successful with unphysical divergence for very simple systems [17]. Also the idea of range separation has been applied to the RPA correlation [7], and interesting functionals including long-range RPA have been developed [5,6,12]. More considerations have included different kernels [exact exchange (EXX) versus Hartree-Fock (HF)] and orbitals (KS versus HF) or the addition of single excitations [13,14], which may improve the description of binding at equilibrium. The RPA is thus believed to be a successful method. It has even been pushed further to tackle big systems [18]. We reveal that this view is incomplete because the RPA method suffers from basic errors, which can be seen and studied in the simplest cases (e.g., $H_2{}^+$ dissociation) and have massive and important implications for larger systems.

Consider the energy of two infinitely separated protons with one and two electrons (i.e. stretched $H_2{}^+$ and stretched H_2). This one problem (the energy of both of these systems) captures an incredible challenge for physics that is not even remotely described by any energy functional in DFT or other methods (HF, MP2), and it is a simple way to phrase the problem of strong correlation. It is thus key to analyze the same energy expression with different numbers of particles, highlighting the connection of distinct chemical species that comes through the use of a single energy functional. A perspective based on fractional numbers of electrons and spins is invoked [19–22], for which exact constraints for the total energy have been derived. The most general flat-plane condition [22] highlights a basic feature of any energy expression, which is its discontinuous derivative at an integer number of electrons, in particular for fractional spin systems. This is violated by all functionals in the literature and remains a challenge.

Testing a method for the flat-plane condition can be done in two ways. It either requires calculating the energy of infinitely stretched systems of integer numbers of protons and electrons with the specified symmetries, or more simply it requires the generalization of the formalism to include occupation numbers and fractional occupations at one dissociated subsystem. A general framework for the extension of any theory explicitly in terms of the one-electron density matrix and one-electron Green function has been developed [23]. This development enables the testing of approximations against exact conditions in a remarkably simple and illuminating manner. It is sufficient to perform calculations on a single hydrogen atom with zero to two electrons. This gives the same information as calculations on many stretched systems (including $H_2{}^+$ and H_2) at the same time. This simple test for RPA reveals massive errors, demanding radically new ideas beyond differentiable functionals of the orbitals and eigenvalues.

Consider the matrix representation of the RPA problem [16]

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \tag{1}$$

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where the matrices $\mathbf{A},\mathbf{B},\mathbf{X},\mathbf{Y}$ are of dimension $n_{\rm occ}n_{\rm virt} \times n_{\rm occ}n_{\rm virt}$, with $n_{\rm occ}$ and $n_{\rm virt}$ being the numbers of occupied and virtual orbitals, respectively, and ω is the $n_{\rm occ}n_{\rm virt}$ vector of excitation energies. The RPA is given by the solution of the above equations in the KS orbital basis with

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ib|aj\rangle, \tag{2}$$

$$B_{ia,jb} = \langle ij|ab\rangle, \tag{3}$$

where ϵ are KS eigenvalues, i,j are occupied orbitals, a,b are virtual orbitals, and $\langle ij|ab\rangle = \int\int \frac{\phi_i(\mathbf{x})\phi_a(\mathbf{x})\phi_j(\mathbf{x}')\phi_b(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{x}d\mathbf{x}'$, where $\mathbf{x}$ is a combined space and spin coordinate. This corresponds to a Hartree-only density response with no exchange-correlation contribution. RPAE (also called RPA + X or full RPA) includes a Hartree-Fock response that requires antisymmetrized integrals in Eqs. (2) and (3) ($\langle ij||ab\rangle = \langle ij|ab\rangle - \langle ij|ba\rangle$) using Hartree-Fock orbitals and eigenvalues.

To extend the method to fractional occupation of the orbitals, the occupation numbers $\{n_p\}$ can be included in the basic matrices using an extension of the fluctuation-dissipation theorem to ensemble Green functions, as proven in Ref. [23]:

$$A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ib|aj\rangle\sqrt{n_i n_j(1-n_a)(1-n_b)}, \tag{4}$$

$$B_{ia,jb} = \langle ij|ab\rangle\sqrt{n_i n_j(1-n_a)(1-n_b)}. \tag{5}$$

The simple rule of generalization to fractional occupations is scaling the orbitals according to their occupation numbers: $\phi_i(\mathbf{x}) \to \sqrt{n_i}\phi_i(\mathbf{x})$ for the occupied orbitals and $\phi_a(\mathbf{x}) \to \sqrt{1-n_a}\phi_a(\mathbf{x})$ for the virtual ones. Also partially occupied orbitals are considered both occupied and virtual, such that now i,j run over $n_{\rm occ} + n_{\rm frac}$; a,b run over $n_{\rm frac} + n_{\rm virt}$; and the dimensionality of the matrices extends to $(n_{\rm occ} + n_{\rm frac})(n_{\rm virt} + n_{\rm frac}) \times (n_{\rm occ} + n_{\rm frac})(n_{\rm virt} + n_{\rm frac})$ for $n_{\rm frac}$, the number of fractionally occupied orbitals. This is consistent with the perspective of fractional charges and spins resulting from dissociation, because at the dissociation limit the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) both become fractional. This is a correct prescription for extending functionals of orbitals to fractional occupations. It gives a correct extension for all the orbital functionals with occupied orbitals [generalized gradient approximation (GGA), HF] but also for MP2 [24] and other many-body theories based on the one-electron Green function [23].

The RPA correlation energy is given by [3,23]

$$E_c^{\rm RPA} = \frac{1}{2}\sum_{ia}(\omega_{ia} - A_{ia,ia}) \tag{6}$$

or [23]

$$E_c^{\rm RPAE} = \frac{1}{4}\sum_{ia}(\omega_{ia} - A_{ia,ia}) \tag{7}$$

with no additional (frequency or coupling constant) integrations and fully expressed in terms of KS quantities. It should be noted that it is also possible to calculate the derivatives $\frac{\partial E}{\partial N}$ by taking derivatives with respect to the frontier orbital occupation number, $\frac{\partial E}{\partial N} = \frac{\partial E_c^{\rm RPA}}{\partial n_f}$, to get the band gap

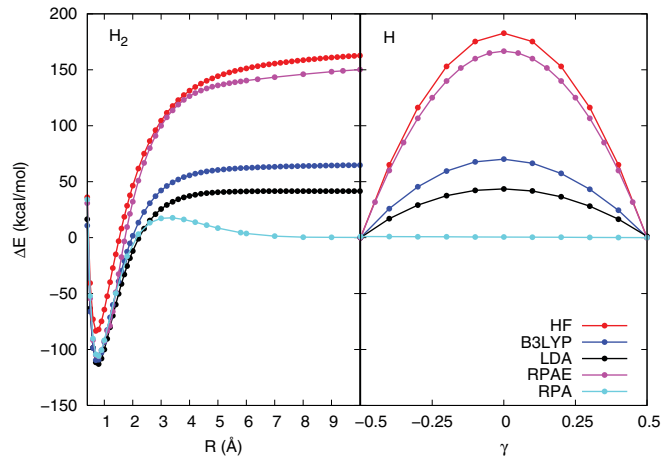

FIG. 1. (Color online) The closed-shell dissociation of H_2 compared with the fractional-spin H atom, $H[n_\alpha,n_\beta]$, $n_\alpha = \frac{1}{2} + \gamma, n_\beta = \frac{1}{2} - \gamma$. All calculations, except Fig. 6, use a cc-pVDZ basis set.

as previously done for MP2 [24] and also discussed in Ref. [23].

We have implemented the above equations in a modified version of CADPAC [25]. We do this by simply calculating the whole $\mathbf{A}$ and $\mathbf{B}$ matrices and then diagonalizing according to Eq. (1) to give the excitation energies. This is computed on top of a Perdew-Burke-Ernzerhof (PBE) calculation using the fractional PBE KS orbitals and eigenvalues (HF in the case of RPAE) to give the total RPA exchange-correlation energy $E_{xc} = E_x^{\rm EXX} + E_c^{\rm RPA}$. This functional could be also treated in a variational fashion using the optimized effective potential method (or its generalized version to accommodate nonlocal potentials in the case of RPAE).

One of the promising aspects of the RPA method is that it greatly improves upon DFAs for the closed-shell dissociation of H_2. This is illustrated in Fig. 1, where the RPA energy is compared with the local density approximation (LDA), the HF method, and the Becke three-parameter Lee-Yang-Parr (B3LYP) approximation [26]. The RPA method predicts the correct dissociation limit, which clearly correlates with the much improved behavior of the hydrogen atom with fractional spins, $H[\frac{1}{2},\frac{1}{2}]$. Remarkably, the RPA method satisfies the constancy condition, and all fractional spin configurations are degenerate in energy and equal to that of the pure-spin H atom with [1,0]. It is possible to study in more detail the energy of the hydrogen atom with general spin occupations, $H[n_\alpha,n_\beta]$, as is shown in Fig. 2. The exact energy should be two flat planes that intersect with a line of discontinuity at $n_\alpha + n_\beta = 1$. We have shown previously [22] that differentiable functionals of the occupied orbitals, such as LDA, GGA, HF, and other hybrid functionals, are unable to qualitatively give this discontinuous behavior of the $E[n_\alpha,n_\beta]$ surface. Other methods involving virtual orbitals such as MP2 or its degenerate corrected version also fail [24]. A simple test on the hydrogen atom shows that the RPA method also qualitatively fails and misses the discontinuity. Therefore, it is expected to fail for problems where this discontinuity is key, such as the band gap of strongly correlated systems.

Very importantly, Fig. 2 reveals another real problem of RPA for the treatment of fractional charges, with an extremely

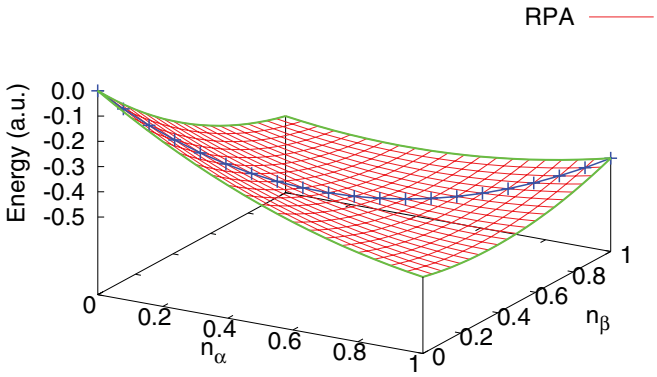

FIG. 2. (Color online) The energy of H[n_α,n_β] for $0 \leqslant n_\alpha \leqslant 1$ and $0 \leqslant n_\beta \leqslant 1$.

convex behavior, much more so than the LDA or other DFAs. To emphasize this erroneous behavior, Fig. 3 shows the dissociation curve of stretched $H_2{}^+$. The result is astonishing: a simple one-electron system where the RPA behaves extremely badly and gives massive correlation energies. Another simple and paradigmatic case, the dissociation of $He_2{}^+$, is considered in Fig. 4. Again the RPA fails dramatically, as shown for the He atom with fractional charges, leading to unphysically low correlation energies that affect not only the dissociation but also the bonding region. Again this error may not be obvious from the underlying RPA equation, but it is revealed by extremely simple tests which highlight many important problems of the method. It is now clear that the RPA method suffers from large delocalization error, which might be due to the lack of an underlying wave function and the poor quality of the Hartree-only response in the RPA. This error is pervasive and can be seen in calculations of many different systems and properties. Thus the positive aspect of the RPA method in the improved description of van der Waals systems such as He_2 gets clouded by the spectacular failure to describe related systems such as $He_2{}^+$.

This analysis may be applied to any method to gain deeper insight into its behavior. For example, RPAE does not suffer from a massive delocalization error (notice the

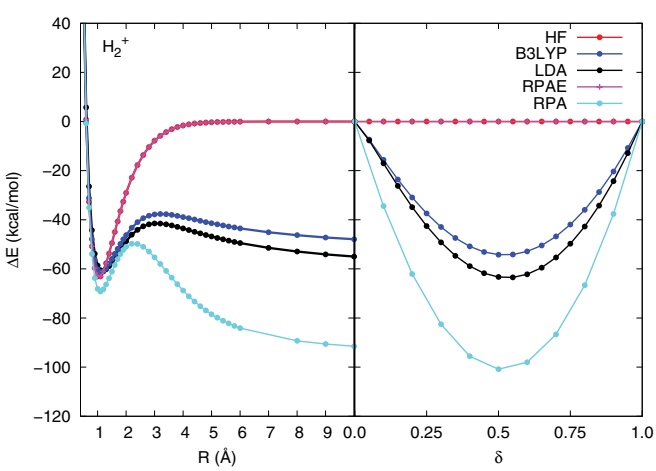

FIG. 3. (Color online) The dissociation of $H_2{}^+$ compared with the fractionally charged H atom, $n_\alpha = \delta, n_\beta = 0$.

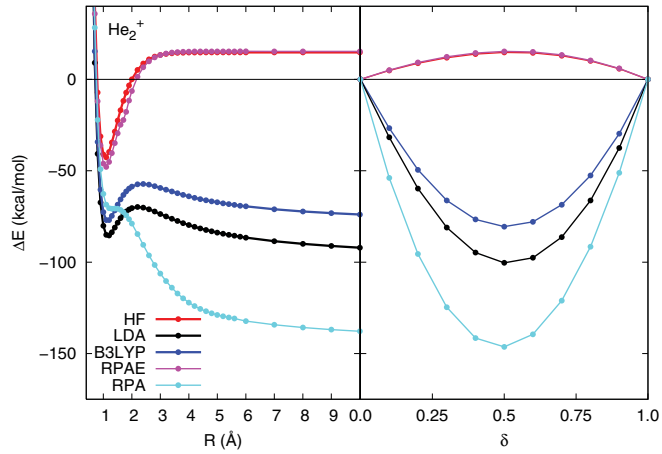

FIG. 4. (Color online) The dissociation of $He_2{}^+$ compared with the fractionally charged He atom, $n_{\alpha,1} = 1, n_{\alpha,2} = 1$; $n_{\beta,1} = 1$, $n_{\beta,2} = \delta$.

improvement over RPA in Figs. 3 and 4) but correspondingly it no longer satisfies the constancy condition, performing worse for fractional spins and hence H_2 dissociation (Fig. 1). This can be clearly seen in the RPAE flat plane of the H atom plotted in Fig. 5, with a much improved description of fractional charges but yet massively violating the constancy condition and lacking the discontinuous behavior. This highlights that it is extremely difficult to improve both aspects at the same time, and in a manner that leads to the flat-plane behavior, for any theory that has a smooth dependence on the occupation numbers.

There has also been much recent interest in including range separation in the RPA ingredients. Following the work of Janesko *et al.* [5] we examine in Fig. 6 the range-separated RPA (rsRPA) functional

$$E_{xc}^{\mathrm{rsRPA}} = E_x^{\mathrm{SR,LDA}} + E_x^{\mathrm{LR,HF}} + E_c^{\mathrm{VWN}} + E_c^{\mathrm{LR,RPA}}, \qquad (8)$$

where a value of $\mu = 1.2$ a.u. is used for the range separation parameter and the $E_x^{\mathrm{SR,LDA}}$ is from Iikura *et al.* [27]. The $E_c^{\mathrm{LR,RPA}}$ is given by the RPA correlation energy with the long-range integrals in Eqs. (2) and (3). This energy is evaluated using PBE orbitals and eigenvalues. Figure 6 clearly illustrates that the effect of range separation is in general to

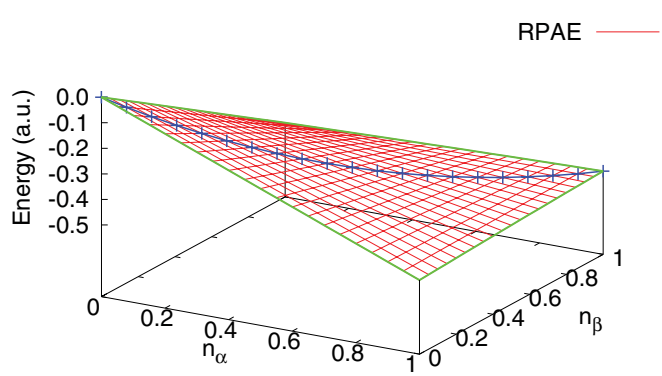

FIG. 5. (Color online) The same as Fig. 2 for RPAE.

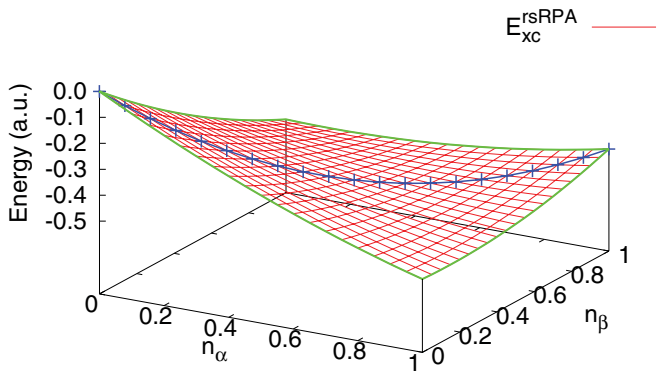

FIG. 6. (Color online) The same as Fig. 2 except for a range-separated RPA functional, Eq. (8), calculated with a 6-31G basis set.

move the surface up, in between RPA and RPAE, such that again the error for fractional charges is decreased, but the good performance for fractional spin deteriorates correspondingly and the constancy condition is no longer fulfilled. There are many other possible methods related to the RPA method [13,14] and the fluctuation-dissipation theorem, such as changing the eigenvalues (KS versus generalized KS) and the kernel (going from RPA to RPAE) [13]. We would recommend that while developing such methods at least stretched $H_2{}^+$ and H_2 are considered, and if the extension to fractional occupations is possible, the flat-plane behavior of Fig. 2 is investigated.

A dramatic failure of the RPA method is seen in the stretching of simple systems, such as $H_2{}^+$, which is understood by considering the extension of the RPA to fractional occupations. Although RPA correlation is a complicated orbital-dependent functional, it still does not have the discontinuous behavior needed to satisfy relevant exact conditions for fractional charge and fractional spin. It is found that the RPA has a small static correlation error but a massive delocalization error. This affects many systems throughout chemistry and physics, from reaction barriers to charge transfer complexes. In fact, the lack of a discontinuous nature means that a reduction of the static correlation error leads to an increased delocalization error, and vice versa. For example with range separation the fractional charge behavior improves (stretched $H_2{}^+$) but the fractional spin behavior (stretched H_2) worsens. The same holds for other proposed extensions or modifications of the method. These basic failures of the RPA method highlight the importance of the exact conditions for the energy to be satisfied by methods in and outside DFT, and furthermore the required complexity is beyond differentiable functionals of the occupied orbitals and eigenvalues.

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