Failure of the random phase approximation correlation energy

Paula Mori-Sánchez, Aron Cohen and Weitao Yang

Department of Chemistry, Duke University, Durham, North Carolina 27708, USA

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The random phase approximation (RPA) to the correlation energy is extended to fractional occupations and its performance examined for exact conditions on fractional charges and fractional spins. RPA satisfies the constancy condition for fractional spins that leads to correct bond dissociation and no static correlation error for H₂ but massively fails for fractional charges, with an enormous delocalization error even for a one-electron system such as H₂⁺. Other methods such as range-separated RPA can reduce this delocalization error but only at the cost of increasing the static correlation error. None of the RPA methods seem to have the discontinuous nature required to satisfy both exact conditions and the full unified condition, emphasizing the need to go further than just smooth functionals of the orbitals.

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 to the RPA [3, 4, 5, 6, 7, 8], highlighted by the work of Furche [3], who has shown a practical way to calculate the correlation energy in the KS context in a similar fashion as in wave function approach [9]. Much of the interest in RPA comes from the improved description of two key aspects for which many other density-functional approximations (DFAs) encounter several problems: One is the description of weak and Van-der-Waals interactions, as typified by molecules such as He₂ or Ne₂; the other is the description of static correlation as seen in the stretching of H₂ [5] and N₂ [10]. Other efforts to include unoccupied orbitals into the exchange-correlation energy, such as MP2 or GL2, have not been so successful with unphysical divergence for very simple systems [11]. Also the idea of range separation has been applied to the RPA correlation [5], and interesting functionals including long-range RPA have been developed [4].

We have recently been attempting to gain insight [12] into the problems of DFAs and other electron correlation methods relating to the delocalization error [13] (fractional charge perspective) and the static correlation error [14] (fractional spin perspective). The combination of these two in a unified condition [15] is much more powerful and highlights a basic property of the exchange-correlation functional, that is its discontinuous derivative at integer number of particles in particular for fractional spin systems. This property is violated by all functionals in the literature and it is key, for example, for the accurate calculation the the band-gap of strongly correlated systems. The performance of a method can be investigated by testing this unified condition for fractional charges and spins, which just requires a generalization of the method to include occupation numbers and fractional occupations as we have done recently for MP2 [16].

This test is remarkably simple and illuminating, as it is sufficient to perform calculations on one-electron systems (e.g. the Hydrogen atom even with one basis function is enough). Our aim in this work is to carry out this simple test for RPA and investigate some of the implications for the method. This understanding offers insight about the largest errors of DFAs, but does not address the weak but very important Van-der-Waals energies.

Consider the matrix representation of the RPA problem [10]

\[
\begin{pmatrix}
A & B \\
-B & -A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
= \omega
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\]

(1)

where the matrices \(A, B, X, Y\) are of dimension \(n_{\text{occ}} \times n_{\text{virt}}\), with \(n_{\text{occ}}\) and \(n_{\text{virt}}\) being the number of occupied and virtual orbitals, and \(\omega\) is the \(n_{\text{occ}} \times n_{\text{virt}}\) vector of excitation energies. RPA is given by the solution of the above equations in the KS orbital basis with

\[
A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ij|ab \rangle
\]

(2)

\[
B_{ia,jb} = \langle ij|ab \rangle
\]

(3)

where \(\epsilon\) are KS eigenvalues, \(i,j\) are occupied orbitals, \(a,b\) are virtual orbitals, and \(\langle ij|ab \rangle = \int \int \frac{\phi_i(x)\phi_a(x')\phi_j(x)\phi_b(x')}{|r-r'|} \, dx \, dx'\) where \(x\) 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 \(\langle ij||ab \rangle = \langle ij|ab \rangle - \langle ij|ba \rangle\) integrals in Eqs. (2).

To extend the method to fractional occupation of the orbitals, the occupation numbers \(n_p\) can be included into the basic matrices using an extension of the fluctuation-dissipation theorem to ensemble density matrices [17]

\[
A_{ia,jb} = (\epsilon_a - \epsilon_i)\delta_{ia,jb} + \langle ij|ab \rangle \sqrt{n_in_j(1-n_a)(1-n_b)}
\]

(4)

\[
B_{ia,jb} = \langle ij|ab \rangle \sqrt{n_in_j(1-n_a)(1-n_b)}.
\]

(5)
Partially occupied orbitals are considered both occupied and virtual, such that now \( i, j \) run over \( n_{\text{occ}} + n_{\text{frac}} \), \( \alpha, \beta \) run over \( n_{\text{frac}} + n_{\text{virt}} \) and the dimensionality of the matrices extends to \((n_{\text{occ}} + n_{\text{frac}})(n_{\text{virt}} + n_{\text{frac}}) \times (n_{\text{occ}} + n_{\text{frac}})(n_{\text{virt}} + n_{\text{frac}})\) for \( n_{\text{frac}} \) number or fractionally occupied orbitals. This is consistent with the perspective of fractional charges and spins resulting from dissociation. At the dissociation limit the HOMO and LUMO both become fractional. This appears to be a correct recipe to extend functionals of orbitals to fractional occupations. It gives a correct extension for all the orbital functionals of occupied orbitals (GGA, HF) and also for MP2. The RPA correlation energy is given by \[3\]

\[ E_c^{\text{RPA}} = \frac{1}{2} \sum_{ia} (\omega_{ia} - A_{ia,ia}) \]  

(6)

with no additional (frequency or coupling constant) integrations and fully expressed in term 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, \( \frac{\partial E}{\partial N} = \frac{\partial E_c^{\text{RPA}}}{\partial n_f} \), to get the band-gap as previously done for MP2 \[10\].

We have implemented the above equations in a modified version of CADPAC. We do this very simply by calculating the whole \( A \) and \( B \) matrices and then diagonalizing according to Eq. \[1\] to give the excitation energies. This is computed post-PBE calculation using the fractional PBE KS orbitals and eigenvalues, to give the total RPA exchange-correlation energy \( E_{xc} = E_{cx}^{\text{EXX}} + E_c^{\text{RPA}} \). 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 for RPAE), but this has not been done in this work.

One of the promising aspects of RPA is that it greatly improves upon DFAs for the closed shell dissociation of H\(_2\). This is illustrated in Fig. \[4\] where the RPA energy is compared with LDA, Hartree-Fock (HF) and B3LYP \[15\]. RPA predicts the correct dissociation limit, which clearly correlates with the much improved behavior of the Hydrogen atom with fractional spins, \( \text{H}[\frac{1}{2}, \frac{1}{2}] \). Remarkably, RPA 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, \( E[n_\alpha, n_\beta] \), 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 \[15\] that smooth functionals of the occupied orbitals, such as LDA, GGA, HF and other hybrid functionals, are unable to qualita-
tively 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 [10]. For RPA, it might not be immediately clear from a consideration of the underlying equations whether the RPA energy has a discontinuity that is sufficient to give the desirable flat plane behavior. A simple test on the Hydrogen atom shows that RPA 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. 3 reveals another real problem of RPA for the treatment of fractional charges, with an extremely convex behavior, much more so than LDA or other DFAs. To emphasize this erroneous behavior, Fig.

Figure 4: The dissociation of He$_2^+$ compared with the fractional charge He atom, $n_{\alpha,1} = 1$, $n_{\alpha,2} = 1$; $n_{\beta,1} = 1$, $n_{\beta,2} = \delta$.

Figure 5: The closed shell dissociation of N$_2$ compared with the fractional spin N atom, $n_{\alpha,1} = 1$, $n_{\alpha,2} = 1$, $n_{\alpha,3} = n_{\alpha,4} = n_{\alpha,5} = (\frac{1}{2} + \gamma)$; $n_{\beta,1} = 1$, $n_{\beta,2} = 1$, $n_{\beta,3} = n_{\beta,4} = n_{\beta,5} = (\frac{1}{2} - \gamma)$.

Figure 6: A fractional spin Carbon atom calculated with $n_{\alpha,1} = 1$, $n_{\alpha,2} = 1$, $n_{\alpha,3} = n_{\alpha,4} = (1 - \frac{4}{3})$, $n_{\alpha,5} = \delta$; $n_{\beta,1} = 1$, $n_{\beta,2} = 1$. The spherical Carbon atom corresponds to $\delta = \frac{1}{2}$.

[3] shows the dissociation curve of stretched H$_2^+$. The result is astonishing, a simple one-electron system where RPA behaves extremely badly and give massive correlation energies. Another simple and paradigmatic case, the dissociation of He$_2^+$ is considered in Fig. 4. Again RPA fails dramatically, as shown for the He 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 equation, but is revealed by extremely simple tests which highlight many important problems of the method. It is now clear that RPA suffers from large delocalization error, which might be due to the lack of an underlying wavefunction and the poor quality of the Hartree-only response in RPA. This error is pervasive and can be seen in calculations of many different systems and properties. Thus the positive aspect of RPA 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$_2^+$.

On a more positive note, we examine the behavior of RPA for some other challenging static correlation error problems. In general, the same improvement seen for H$_2$ carries over to more complex systems, such as N$_2$ in Fig. 5, where RPA is still very close to satisfying the constancy condition for multiple fractional spins. Fig. 6 considers the slightly different static correlation problem of the spatial degeneracy within the $p$ set, as exemplified by the massive error of HF for an spherical atom against a non-spherical atom. In this case RPA makes a large correction to HF, and rather interestingly, it even makes the spherical atom slightly lower in energy, in contrast to most methods. These two positive aspects show that RPA deals well with this type of spin and spatial degeneracy and makes it a very interesting prospect to tackle more
challenging problems of transition metal chemistry.

This analysis should be applied to any method to gain a deeper insight into its behavior. For example RPAE may not suffer from a massive delocalization error but correspondingly it would no longer satisfy the constancy condition, performing worse for fractional spins and hence $H_2$ dissociation. It is extremely difficult to improve both aspects at the same time and in a manner that leads to the flat plane behavior. There has also been much recent interest in including range-separation into the RPA ingredients. Following the work of Janesko et al. [4] we examine in Fig. 7

$$E_{xc} = E^{SR, LDA}_x + E^{LR, HF}_x + E^{VWN}_c + E^{LR, RPA}_c$$

(7)

where a value of $\mu = 1.2$ a.u. is used for the range separation parameter and the $E^{SR, LDA}_x$ is from Iikura et al. [19]. The $E^{LR, RPA}_c$ is RPA with the long-range integrals in Eqs. 2-4. This energy is evaluated using PBE orbitals and eigenvalues. Fig. 7 clearly illustrates that the effect of range separation is in general to move the surface up such that the error for fractional charges is decreased, however the good performance for fractional spin deteriorates correspondingly and the constancy condition is no longer fulfilled. There are many other possibilities in methods related to RPA and the fluctuation-dissipation theorem, such as changing the eigenvalues (KS versus generalized KS) and the kernel (going from RPA to RPAE).

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.

We have investigated the behavior of some RPA based methods for the extension to fractional charges and fractional spins, to give insight into their performance for harder challenges in theoretical chemistry. Although RPA correlation is a complicated orbital dependent functional, it still does not have the discontinuous behavior needed to satisfy both the exact conditions for fractional charge and fractional spin. RPA has a much reduced static correlation error but has a massive delocalization error. In fact, the lack of discontinuous nature means that an improved performance for fractional spins likely leads to a much worse performance for fractional charges, and vice versa. For example with range separation the fractional charge behavior improves but the dissociation limit of $H_2$ worsens. The main purpose of this work is to highlight the importance of the exact conditions on the energy to be satisfied by methods in and outside DFT, and the complexity that is needed may not be covered easily by functionals of the unoccupied orbitals and eigenvalues.

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