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INVITED ARTICLE

The connection between self-interaction and static correlation: a random phase approximation perspective

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Semi-local density functional theory suggests a connection between static correlation and self-interaction. It is difficult to make such a connection from the wave function theory perspective, since few wave function methods permit self-interaction error. However, the random phase approximation for ground-state correlation, which has a wave function derivation, does include self-interaction in its direct (Hartree) variant. This variant also describes left–right correlation. The self-interaction can be removed by means of second-order screened exchange; however, this also has negative consequences for the description of static correlation. This paper discusses the connection between the two concepts (static correlation and self-interaction) from the perspective provided by the random phase approximation.

Keywords: static correlation; self-interaction; random phase approximation

1. Introduction

One of the many strengths of Kohn–Sham (KS) density functional theory (DFT) [1–3] is that it can, at the mean-field level, mimic some of the effects of static correlation (i.e. correlation between the reference determinant and determinants degenerate to it) even though from the wave function perspective, the presence of static correlation would tend to indicate that the single-determinant reference is qualitatively incorrect.

The mechanism by which KS-DFT accomplishes this feat is well understood [4,5]. When left–right static correlation is important, the exact exchange hole delocalises across the system, with compensating delocalisation of the correlation hole such that the exchange-correlation hole localises around the reference electron. The model exchange-correlation holes used in standard semi-local density functionals are localised around the reference electron by construction, and thus carry physics similar to that of the exact exchange-correlation hole.

On the other hand, the exchange-correlation hole from semi-local functionals is not localised for the proper reasons. Instead of compensating delocalised exchange and correlation pieces, the KS-DFT exchange-correlation hole is built from a localised exchange hole and a localised correlation hole. One consequence of this is that the self-exchange interaction is not correctly described and, in particular,

it does not cancel with the self-Coulomb interaction. Additionally, most of these typical functionals allow electrons to correlate with themselves as well. In other words, the same exchange-correlation functionals which mimic static correlation also carry self-interaction [6]. Note that for most of this work, we use ‘self-interaction’ to refer to one-electron self-interaction error, and not to many-electron self-interaction error [7,8].

The quantum chemistry community has long realised that while static correlation and self-interaction *seem* unrelated, they are at least qualitatively connected. But frustratingly, it is not straightforward to establish a formal relation between the two. The purpose of this article is to show an explicit connection between static correlation and self-interaction error in the random phase approximation (RPA) [9–14] for ground-state correlation. Section 2 reviews RPA and includes our discussions of self-interaction and static correlation within the random phase approximation. Some sample results are given in Section 3, and conclusions are drawn in Section 4.

2. The random phase approximation

The random phase approximation in the plasmonic formulation extracts the ground-state correlation energy of a system as the difference in zero-point

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energies from two excitation problems, one correlated and the other uncorrelated.

The correlated excitation problem is essentially time-dependent linear response, and one solves

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} = \begin{pmatrix} \mathbf{X} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{X} \end{pmatrix} \begin{pmatrix} \boldsymbol{\omega} & \mathbf{0} \\ \mathbf{0} & -\boldsymbol{\omega} \end{pmatrix}, \quad (1)$$

where the matrices \mathbf{A} , \mathbf{B} , \mathbf{X} , and \mathbf{Y} are all $ov \times ov$, with o and v respectively the number of occupied and unoccupied spin-orbitals. The excitation energies $\boldsymbol{\omega}$ are chosen to be non-negative.

The uncorrelated excitation problem simply involves making the Tamm–Dancoff approximation (commonly known as configuration interaction singles), in which one sets $\mathbf{B} = \mathbf{0}$ and recovers simply

$$\mathbf{A}\mathbf{Z} = \mathbf{Z}\mathbf{v}. \quad (2)$$

The correlation energy is then simply [10]

$$E_c^{\text{RPA}} = \frac{1}{2} \text{Tr}(\boldsymbol{\omega} - \mathbf{v}) = \frac{1}{2} \text{Tr}(\boldsymbol{\omega} - \mathbf{A}). \quad (3)$$

Different variants of RPA differ in the definitions of the matrices \mathbf{A} and \mathbf{B} . Roughly speaking, matrix elements of \mathbf{A} correspond to matrix elements of the Hamiltonian between two singly-excited determinants, while matrix elements of \mathbf{B} correspond to matrix elements of the Hamiltonian between the reference determinant and a doubly-excited determinant. In what we call the ‘direct RPA’ (dRPA) variant, the matrices \mathbf{A} and \mathbf{B} are given by

$$A_{ia,jb} = \langle ib|aj \rangle + (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab}, \quad (4a)$$

$$B_{ia,jb} = \langle ij|ab \rangle, \quad (4b)$$

in terms of orbital energies ϵ and two-electron integrals in Dirac notation:

$$\langle pq|rs \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \varphi_p^*(\mathbf{x}_1)\varphi_q^*(\mathbf{x}_2) \frac{1}{r_{12}} \varphi_r(\mathbf{x}_1)\varphi_s(\mathbf{x}_2) \quad (5)$$

where \mathbf{x} is a space-spin coordinate. Indices $i, j, k \dots$ indicate occupied orbitals, while $a, b, c \dots$ indicate unoccupied orbitals, so the compound index ia refers to single excitations. Note that if one has real orbitals, then in dRPA we have

$$\mathbf{A} = \mathbf{B} + \Delta\boldsymbol{\epsilon}, \quad (6)$$

where $\Delta\boldsymbol{\epsilon}$ is a diagonal matrix of orbital energy differences.

2.1. The RPA as an approximate coupled-cluster method

While the plasmonic formulation of RPA has a simple conceptual appeal, one can also formulate the method

in a seemingly different approach, as a particularly simple approximate coupled-cluster method [14–16]. The ring diagrams (particle–hole contractions, essentially) can be summed to infinite order if one solves the Riccati equation

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = \mathbf{0} \quad (7)$$

for the RPA amplitudes \mathbf{T} . The correlation energy can then be obtained from

$$E_c^{\text{dRPA}} = \frac{1}{2} \text{Tr}(\mathbf{B}\mathbf{T}). \quad (8)$$

Note that there is some discussion about the appropriate definition of the correlation energy in full RPA (also known as RPA with exchange), in which the two-electron integrals in \mathbf{A} and \mathbf{B} are antisymmetrised [9,17].

While the two formulations of RPA have long been known in the literature, we recently provided a simple analytic demonstration of their equivalence [14]. One has

$$\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1} \quad (9)$$

and finds that

$$\text{Tr}(\mathbf{B}\mathbf{T}) = \text{Tr}(\boldsymbol{\omega} - \mathbf{A}). \quad (10)$$

We note in passing that the Riccati equation has multiple solutions, and in particular that if \mathbf{T} is a solution, so too is \mathbf{T}^{-1} , with

$$\text{Tr}(\mathbf{B}\mathbf{T}^{-1}) = \text{Tr}(-\boldsymbol{\omega} - \mathbf{A}). \quad (11)$$

Our implementation of RPA is in this coupled-cluster language, and some care should be taken to ensure that the RPA solution one has found corresponds to the plasmonic result.

2.2. Self-interaction in the RPA

Because direct RPA includes only the direct term in the two-electron integrals, it has self-interaction error. That is, a one-electron system should have $\mathbf{T} = \mathbf{0}$ and $E_c = 0$, and neither is the case with direct RPA. This self-interaction can be removed from the energy (but not the wave function) by the second-order screened exchange (SOSEX) approximation [15,18,19], in which one solves the dRPA equations for \mathbf{T} but then obtains the correlation energy from

$$E_c^{\text{SOSEX}} = \frac{1}{2} \text{Tr}((\mathbf{B} - \mathbf{K})\mathbf{T}), \quad (12)$$

where

$$\mathbf{K}_{ia,jb} = \langle ij|ba \rangle. \quad (13)$$

For one-electron systems, $\mathbf{B} = \mathbf{K}$ and the correlation energy is thus zero even though the dRPA amplitudes are not. For two-electron singlets, the same-spin block of \mathbf{K} and the same-spin block of \mathbf{B} are identical and SOSEX gives half the dRPA correlation energy. For many-electron systems, the best that can be said is that the diagonal elements of $\mathbf{B} - \mathbf{K}$ vanish.

We should also point out that SOSEX can also be described by first solving the dRPA equations for \mathbf{T} but then antisymmetrising it:

$$\tilde{\mathbf{T}}_{ia,jb} = \mathbf{T}_{ia,jb} - \mathbf{T}_{ib,ja}. \quad (14)$$

The correlation energy is then

$$E_c^{\text{SOSEX}} = \frac{1}{4} \text{Tr}(\tilde{\mathbf{B}}\tilde{\mathbf{T}}), \quad (15)$$

where we have written

$$\tilde{\mathbf{B}}_{ia,jb} = \mathbf{B}_{ia,jb} - \mathbf{B}_{ib,ja} = \mathbf{B}_{ia,jb} - \mathbf{K}_{ia,jb}. \quad (16)$$

This formulation also removes the self-interaction from the wave function, in the sense that $\tilde{\mathbf{T}} = \mathbf{0}$ for one-electron systems. Little attention has been paid to the proper way of defining SOSEX, and in our opinion this latter formulation is more correct.

2.3. Closed-shell RPA

Because we are interested primarily in a discussion of left–right correlation, which implies using a closed-shell reference, it is helpful to work in a closed-shell formulation of RPA.

Partitioning a generic matrix \mathbf{M} as

$$\mathbf{M} = \begin{pmatrix} \mathbf{M}_{\uparrow\uparrow} & \mathbf{M}_{\uparrow\downarrow} \\ \mathbf{M}_{\downarrow\uparrow} & \mathbf{M}_{\downarrow\downarrow} \end{pmatrix}, \quad (17)$$

we write the matrices \mathbf{A} , \mathbf{B} , \mathbf{K} , and \mathbf{T} as

$$\mathbf{A} = \begin{pmatrix} \mathbf{a} + \delta\epsilon & \mathbf{a} \\ \mathbf{a} & \mathbf{a} + \delta\epsilon \end{pmatrix}, \quad (18a)$$

$$\mathbf{B} = \begin{pmatrix} \mathbf{b} & \mathbf{b} \\ \mathbf{b} & \mathbf{b} \end{pmatrix}, \quad (18b)$$

$$\mathbf{K} = \begin{pmatrix} \mathbf{k} & \mathbf{0} \\ \mathbf{0} & \mathbf{k} \end{pmatrix}, \quad (18c)$$

$$\mathbf{T} = \begin{pmatrix} \mathbf{p} & \mathbf{q} \\ \mathbf{q} & \mathbf{p} \end{pmatrix}, \quad (18d)$$

with

$$a_{IA,JB} = \langle IB|AJ \rangle, \quad (19a)$$

$$b_{IA,JB} = \langle IJ|AB \rangle, \quad (19b)$$

$$(\delta\epsilon)_{IA,JB} = (\epsilon_A - \epsilon_I)\delta_{IJ}\delta_{AB}, \quad (19c)$$

$$k_{IA,JB} = \langle IJ|BA \rangle, \quad (19d)$$

where indices I , J , A , and B refer to spatial orbitals.

The same-spin and opposite-spin blocks of the Riccati equations become, respectively,

$$\mathbf{0} = \mathbf{b} + \mathbf{a}(\mathbf{p} + \mathbf{q}) + \delta\epsilon\mathbf{p} + (\mathbf{p} + \mathbf{q})\mathbf{a} + \mathbf{p}\delta\epsilon \\ + (\mathbf{p} + \mathbf{q})\mathbf{b}(\mathbf{p} + \mathbf{q}), \quad (20a)$$

$$\mathbf{0} = \mathbf{b} + \mathbf{a}(\mathbf{p} + \mathbf{q}) + \delta\epsilon\mathbf{q} + (\mathbf{p} + \mathbf{q})\mathbf{a} + \mathbf{q}\delta\epsilon \\ + (\mathbf{p} + \mathbf{q})\mathbf{b}(\mathbf{p} + \mathbf{q}). \quad (20b)$$

Adding these two equations and writing $\mathbf{t} = \mathbf{p} + \mathbf{q}$, we find

$$\mathbf{0} = \mathbf{b} + \left(\mathbf{a} + \frac{1}{2}\delta\epsilon\right)\mathbf{t} + \mathbf{t}\left(\mathbf{a} + \frac{1}{2}\delta\epsilon\right) + \mathbf{t}\mathbf{b}\mathbf{t}. \quad (21)$$

Subtracting the two equations instead gives us

$$\mathbf{0} = \delta\epsilon(\mathbf{p} - \mathbf{q}) + (\mathbf{p} - \mathbf{q})\delta\epsilon. \quad (22)$$

Inserting the definition of $\delta\epsilon$ and noting that $\delta\epsilon$ is diagonal, this is simply

$$0 = (\epsilon_A + \epsilon_B - \epsilon_I - \epsilon_J)(p_{IA,JB} - q_{IA,JB}) \quad (23)$$

with the obvious solution that $\mathbf{p} = \mathbf{q}$. In cases when the orbital energy difference vanishes, any choice for $\mathbf{p} - \mathbf{q}$ will do and we may still select $\mathbf{p} = \mathbf{q}$.

Thus, in the closed shell case we have

$$\mathbf{T} = \frac{1}{2} \begin{pmatrix} \mathbf{t} & \mathbf{t} \\ \mathbf{t} & \mathbf{t} \end{pmatrix} \quad (24)$$

and we obtain \mathbf{t} by solving Equation (21), which looks just like the standard Riccati equation except that one takes only half the orbital energy difference and works with spatial orbitals. The correlation energies in dRPA and SOSEX work out to be, respectively,

$$E_c^{\text{dRPA}} = \text{Tr}(\mathbf{b}\mathbf{t}), \quad (25a)$$

$$E_c^{\text{SOSEX}} = \text{Tr}(\mathbf{b}\mathbf{t}) - \frac{1}{2} \text{Tr}(\mathbf{k}\mathbf{t}). \quad (25b)$$

2.4. Static correlation in the RPA

Let us now consider a closed-shell system in which the orbitals are real and all the orbitals are degenerate (thus, $\delta\epsilon = \mathbf{0}$ and $\mathbf{a} = \mathbf{b}$). In a typical

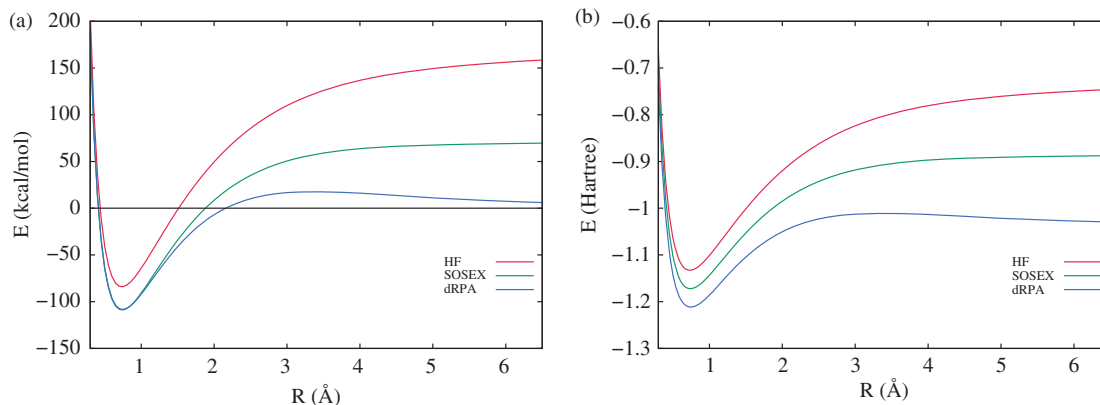


Figure 1. Dissociation of H₂ with dRPA and SOSEX. (a) Dissociation relative to two hydrogen atoms. (b) Dissociation on an absolute energy scale.

molecular calculation, this might be achieved with a suitable active space. Since all the orbitals are degenerate, the correlation in this limit is purely static in nature. In this special case, the dRPA equation is

$$(\mathbf{1} + \mathbf{t})\mathbf{b}(\mathbf{1} + \mathbf{t}) = \mathbf{0}. \quad (26)$$

When \mathbf{b} is positive definite, the only solution is $\mathbf{t} = -\mathbf{1}$ and the dRPA and SOSEX correlation energies are then, respectively,

$$E_c^{\text{dRPA}} = -\langle IA|IA \rangle, \quad (27a)$$

$$E_c^{\text{SOSEX}} = -\frac{1}{2}\langle IA|IA \rangle. \quad (27b)$$

If \mathbf{b} has any zero eigenvalues, then some components of \mathbf{t} are not well defined, but these components do not contribute to the correlation energy.

If we further specialise to the case of left–right correlation for two identical atoms at infinite separation, for which $\langle IA|IA \rangle = \langle II|II \rangle$, the dRPA correlation energy is exactly correct and is equal to twice the atomic self-interaction error, while the SOSEX correlation energy is too small by a factor of two. That is, dRPA has both self-interaction and static correlation, and SOSEX removes the former but in the course of doing so also reduces the latter. This is a clear illustration of the connection between static correlation and self-interaction from a wave function perspective.

3. Results

While the results we have discussed so far – that SOSEX recovers only half of the static correlation energy – are only true in special cases, the general conclusion that SOSEX greatly reduces the static

correlation energy over dRPA remains true. We illustrate this with several examples.

All our calculations are done in the development version of Gaussian [20], using the aug-cc-pVQZ [21–23] basis set with no counterpoise correction unless otherwise noted. Because dRPA is most correctly done from a semi-local reference [11,24,25], we use PBE orbitals and orbital energies. Curves labelled ‘HF’ report the expectation value of the Hamiltonian with respect to the PBE determinant (in other words, the Hartree–Fock energy expression with PBE orbitals), while those labelled ‘SOSEX’ and ‘dRPA’ respectively add to this the SOSEX or dRPA correlation energies of Equation (25).

Figure 1 shows the dissociation curve for H₂, for which, as is well established, dRPA dissociates correctly [12]. As is typically the case, dRPA and SOSEX are superimposable at equilibrium, but SOSEX recovers only a fraction of the static correlation at dissociation. It might appear that SOSEX recovers slightly more than half of the static correlation energy. This is simply due to the fact that SOSEX and dRPA give different results for the hydrogen atom, which dRPA predicts to have a non-zero correlation energy. On an absolute energy scale, as shown in Figure 1(b), one can see that SOSEX captures exactly half of the dRPA correlation energy for all bond lengths, as expected.

A more useful test case is provided by N₂, for which, in the separated atom limit, there are multiple unoccupied orbitals at the Fermi level. Figure 2 shows the dissociation for N₂. While SOSEX and dRPA are again superimposable at equilibrium, it is clear that SOSEX recovers only a small fraction of the static correlation energy at dissociation. On the absolute energy scale, we see that SOSEX recovers rather more

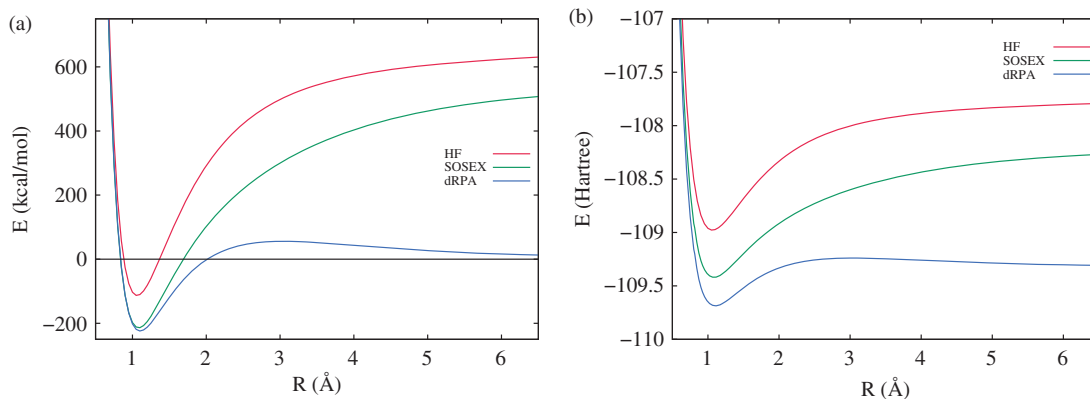


Figure 2. Dissociation of N₂ with dRPA and SOSEX. (a) Dissociation relative to two nitrogen atoms. (b) Dissociation on an absolute energy scale.

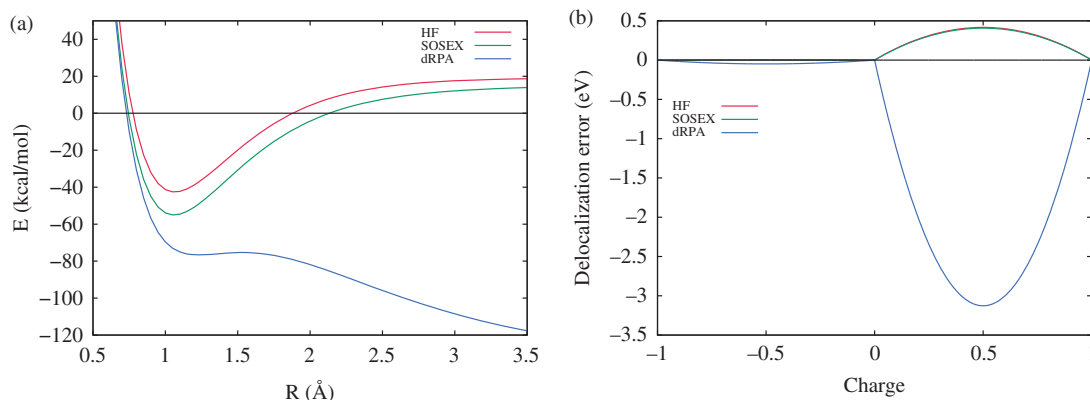


Figure 3. Many-electron self-interaction error in helium systems from dRPA and SOSEX. (a) Dissociation of He₂⁺ by dRPA and SOSEX. (b) Delocalisation error in helium from dRPA and SOSEX.

than half of the dRPA correlation energy near equilibrium and far less than half near dissociation.

We point out the small bumps in the dRPA dissociation curves; these bumps are endemic to dRPA, but removed by SOSEX. Presumably, the bump has something to do with the self-interaction in dRPA. This is not the only benefit of eliminating the one-electron self-interaction error. A separate important feature is that SOSEX also reduces the enormous many-electron self-interaction error [7,8] from which dRPA suffers. One consequence of this is that SOSEX can more properly dissociate homonuclear diatomic ions than can dRPA. Yang and co-workers define the delocalisation error [26] as

$$2\Delta E_{\text{deloc}} = E(X_2^\pm) - E(X) - E(X^\pm), \quad (28)$$

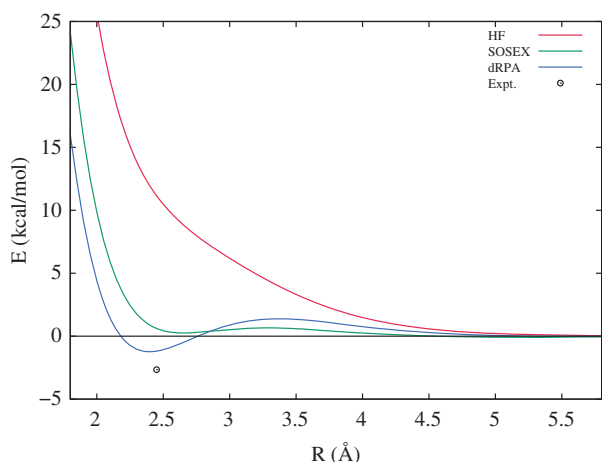
where the energy of the diatomic ion is taken at infinite separation. The delocalisation error measures the

extent to which a method favours or disfavors an electronically delocalised state which could be described as $2 X^{\pm 1/2}$ over the electronically localised state of $X + X^\pm$. The left panel of Figure 3 shows the dissociation curve for He₂⁺, while the right panel shows the delocalisation error for helium. As promised, SOSEX dramatically improves upon dRPA for these types of dissociations, though it does not improve upon the delocalisation error (and hence the many-electron self-interaction error) present in the Hartree–Fock energy expression. This is in marked contrast to more accurate wave function methods, as illustrated by Table 1.

While dRPA does describe left–right static correlation correctly, albeit at the cost of an unphysical bump in the dissociation curve, it does not describe all forms of static correlation exactly. This is readily seen by considering the beryllium dimer. This system is weakly bound, with the characteristic

Table 1. Delocalisation errors (meV) from several methods.

	He ₂ ⁺	He ₂ ⁻	Ne ₂ ⁺	Ne ₂ ⁻
HF	416	4	872	30
dRPA	-3127	-48	-2528	-593
SOSEX	407	2	898	-2
CCSD	5	0	79	2
CCSD(T)	1	0	10	0

Figure 4. Dissociation of Be₂ with dRPA and SOSEX.

near-degeneracies between $2s$ and $2p$ orbitals of beryllium atoms. The experimental dissociation energy and bond length are 929.7 cm^{-1} and 2.454 \AA , respectively [27]. Even high-level calculations yield a fairly broad dispersion in the results [28–36], but are qualitatively able to reproduce the binding. This does not seem to be true either of dRPA or of SOSEX, judging by Figure 4. These calculations are counterpoise corrected and basis set extrapolated [37–39] from the aug-cc-pVQZ and aug-cc-pV5Z results. In this case, neither Hartree–Fock nor SOSEX give bound curves, and while dRPA has some binding, it is clearly inadequate for the description of Be₂. Fuchs and Gonze [40] also considered the dissociation of Be₂ with dRPA. Their calculations agree with ours in finding that dRPA underbinds Be₂, although they find the underbinding to be less severe than we do. The origins of this discrepancy presumably have to do with basis set effects. In this regard it is worth noting that even with basis set extrapolation, counterpoise correction noticeably reduces the binding energy in our calculations.

4. Conclusions

That static correlation and self-interaction are in some sense related (or, more precisely, that left–right static

correlation and self-interaction are related) seems fairly clear. It is frustratingly difficult to pin down the relation analytically; this is no doubt due in part to the fact that essentially any meaningful wave function method has no one-electron self-interaction error. However, direct RPA can be thought of as a particularly simple wave function method whose extension to SOSEX removes the one-electron self-interaction error, reduces the many-electron self-interaction error, but also worsens the description of left–right correlation.

Because SOSEX does offer significant improvement in many ways, we believe that the optimal dRPA-type method would include some fraction of the exchange that SOSEX adds to dRPA (though perhaps not all of it). While admixing some part of SOSEX with dRPA will inevitably degrade the performance for left–right correlation and thus presumably worsen thermochemistry, the benefits in terms of reduced one- and many-electron self-interaction error could be sizable.

Acknowledgements

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Appendix 1. Solving the dRPA Equations

Solving the RPA equations as \mathbf{A} approaches \mathbf{B} (that is, as the orbital energy gap goes to zero) can be somewhat challenging. Our approach is essentially a pseudo-Newton method.

Recall that the RPA equation is

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = \mathbf{0}. \quad (29)$$

We define the residual matrix $\mathbf{R}(\mathbf{T})$ and the gradient matrix $\mathbf{G}(\mathbf{T})$ as

$$\mathbf{R}(\mathbf{T}) = \mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T}, \quad (30a)$$

$$\mathbf{G}(\mathbf{T}) = \mathbf{A} + \mathbf{B}\mathbf{T}. \quad (30b)$$

Then given an initial guess \mathbf{T}_0 , the correction to it $\delta\mathbf{T}$ obeys

$$\mathbf{R}(\mathbf{T}_0) + \delta\mathbf{T}\mathbf{G}(\mathbf{T}_0) + \mathbf{G}^T(\mathbf{T}_0)\delta\mathbf{T} + \delta\mathbf{T}\mathbf{B}\delta\mathbf{T} = \mathbf{0}. \quad (31)$$

Neglecting the term of order $\delta\mathbf{T}^2$ and making the approximation that the gradient is diagonal dominant, we write

$$\delta T_{ia,jb} = -\frac{R_{ia,jb}}{G_{ia,ia} + G_{jb,jb}}. \quad (32)$$

In order to further assist convergence, we then take

$$\mathbf{T}_0 \rightarrow \mathbf{T}_0 + \alpha\delta\mathbf{T} \quad (33)$$

where α is chosen to minimise $\text{Tr}(\mathbf{R}(\mathbf{T}_0 + \alpha\delta\mathbf{T})^2)$. In the limiting case that \mathbf{T} is a number instead of a matrix, we thus converge in one iteration; convergence for larger dimensions is much faster than we would obtain in the usual case where we instead write

$$\delta T_{ia,jb} = -\frac{R_{ia,jb}}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}, \quad (34)$$

where the ϵ 's are orbital energies (and are a part of \mathbf{G} , since they contribute to \mathbf{A}).