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## Long-range-corrected hybrids including random phase approximation correlation

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We recently demonstrated a connection between the random phase approximation (RPA) and coupled cluster theory [G. E. Scuseria *et al.*, *J. Chem. Phys.* **129**, 231101 (2008)]. Based on this result, we here propose and test a simple scheme for introducing long-range RPA correlation into density functional theory. Our method provides good thermochemical results and models van der Waals interactions accurately. © 2009 American Institute of Physics.

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### I. INTRODUCTION

We recently demonstrated that the ground state correlation energy associated with the random phase approximation (RPA)<sup>1–8</sup> is connected with an approximate ring coupled cluster doubles (rCCD) approach. The RPA excitation problem requires the solution of

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

where the matrices  $\mathbf{A}$ ,  $\mathbf{B}$ ,  $\mathbf{X}$ , and  $\mathbf{Y}$  are of dimension  $ov \times ov$ , with  $o$  and  $v$  being the number of occupied and unoccupied spin-orbitals, respectively. The plasmonic formula<sup>2</sup> for the RPA ground state correlation energy is

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

As shown in our previous paper,<sup>8</sup> Eq. (1) is equivalent to

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = 0, \quad (3)$$

an approximate coupled cluster doubles equation with excitation amplitudes  $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$ . Further, the RPA correlation energy can be evaluated from the CC-like expression

$$E_c^{\text{rCCD}} = \frac{1}{2} \text{Tr}(\mathbf{B}\mathbf{T}) = \frac{1}{2} \text{Tr}(\boldsymbol{\omega} - \mathbf{A}). \quad (4)$$

The excitation amplitudes  $\mathbf{T}$  imply the existence of an underlying wave function in RPA. This lets us follow Stoll and Savin<sup>9</sup> and Savin<sup>10</sup> and introduce range separation between density functional theory (DFT) and wave function theory with RPA for the long-range (LR) correlation. Range separation is a powerful technique<sup>11–19</sup> that can improve upon both standard wave function methods and semilocal exchange-correlation (xc) functionals. Range-separated DFT partitions the electron-electron interaction operator into short range (SR) and LR components as

$$\frac{1}{r_{12}} = \underbrace{\frac{\text{erfc}(\boldsymbol{\omega}r_{12})}{r_{12}}}_{\text{SR}} + \underbrace{\frac{\text{erf}(\boldsymbol{\omega}r_{12})}{r_{12}}}_{\text{LR}}, \quad (5)$$

and typically (but not always; see Refs. 13 and 19) treats the SR (LR) component with semilocal (wave function) approximations.

Toulouse *et al.*<sup>20</sup> recently proposed a range-separated treatment of RPA via the adiabatic connection fluctuation-dissipation theorem,<sup>3,5,21</sup> combining a SR semilocal xc functional with LR full RPA. Consistent with other works,<sup>17,18</sup> they found that their LR correlation energy has a relatively weak basis set dependence. They also removed some artifacts of full-range RPA, including a “bump” in the symmetry-restricted singlet  $\text{Be}_2$  dissociation curve.

### II. THEORY

We propose a simpler LR RPA based on the connection to CC theory discussed above, which avoids a costly adiabatic connection integral. We evaluate LR RPA as a one-shot correction to a self-consistent generalized Kohn–Sham<sup>22</sup> (GKS) calculation combining LR exact [Hartree–Fock-type (HF)] exchange and SR local spin density approximation (LSDA) xc. Our xc energy is

$$E_{\text{xc}} = E_{\text{xc}}^{\text{SR-LSDA}} + E_x^{\text{LR-HF}} + c_{\text{RPA}} E_c^{\text{LR-RPA}}. \quad (6)$$

We evaluate  $E_c^{\text{LR-RPA}}$  with Eqs. (3) and (4) and build  $\mathbf{A}$  and  $\mathbf{B}$  from the LR two-electron integrals and the GKS spin-orbitals and orbital energies. The coefficient  $c_{\text{RPA}}$  is discussed below.

In this work, we focus on what we will refer to as direct RPA. In the (real) canonical spin-orbital basis we use throughout this paper, the direct RPA matrices are

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + \langle ib|aj \rangle, \quad (7a)$$

$$B_{ia,jb} = \langle ij|ab \rangle. \quad (7b)$$

Here  $\epsilon$  is a GKS orbital energy. Indices  $i$  and  $j$  indicate occupied spin-orbitals,  $a$  and  $b$  indicate virtual spin-orbitals, and  $\langle ij|ab \rangle$  is a two-electron integral in Dirac’s notation. For real orbitals, note that  $\langle ib|aj \rangle = \langle ij|ab \rangle$ . What we refer to as full RPA uses antisymmetrized two-electron integrals in Eq. (7).

For practical calculations, direct RPA has the great advantage that the correlation energy is guaranteed to be real if

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the orbitals obey the Aufbau principle. This is not true of full RPA, where instabilities in the reference determinant<sup>23</sup> can produce a complex correlation energy.<sup>3</sup> In cases such as Be<sub>2</sub> where the reference has triplet instabilities,<sup>24</sup> one may have to limit full RPA to singlet excitations, while with direct RPA no such restriction is needed.

An additional advantage of direct RPA is that it reduces the dimension of the problem compared to full RPA (rCCD with antisymmetrized two-electron integrals). Consider the block of  $\mathbf{B}$  corresponding to spatial orbitals  $\varphi_I$ ,  $\varphi_A$ ,  $\varphi_J$ , and  $\varphi_B$  and spin ordering  $\alpha\alpha$ ,  $\beta\beta$ ,  $\alpha\beta$ , and  $\beta\alpha$ . The  $\mathbf{B}$  matrix for full RPA and closed shells becomes

$$\mathbf{B}_{IA..JB} = \begin{pmatrix} \mathcal{J} - \mathcal{K} & \mathcal{J} & 0 & 0 \\ \mathcal{J} & \mathcal{J} - \mathcal{K} & 0 & 0 \\ 0 & 0 & 0 & -\mathcal{K} \\ 0 & 0 & -\mathcal{K} & 0 \end{pmatrix}, \quad (8)$$

with  $\mathcal{J} = \langle IJ|AB \rangle$  and  $\mathcal{K} = \langle IJ|BA \rangle$ . For open shells (unrestricted), the  $\mathcal{J}$  and  $\mathcal{K}$  entries in different blocks will generally differ. Direct RPA ( $\mathcal{K} = 0$ ) zeros the “spin-flip” block of  $\mathbf{B}$  containing only  $-\mathcal{K}$ , reducing the dimension by a factor of two compared to full RPA. For both closed and open shell systems, we can diagonalize the remaining upper block of  $\mathbf{B}$  with the unitary transformation

$$\mathbf{Q} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}. \quad (9)$$

For closed shells,  $\mathbf{Q}$  is a spin-adaptation operator. The resulting  $2 \times 2$  diagonal matrix for direct RPA has only one non-zero eigenvalue, corresponding to singlet excitations. Since only the singlet block of  $\mathbf{B}$  is nonzero, we only need the singlet part of  $\mathbf{T}$  to evaluate the correlation energy of Eq. (4). Additionally, in blocks where  $\mathbf{B} = \mathbf{0}$  the ring CCD equation (Eq. (3)) becomes

$$\mathbf{AT} + \mathbf{TA} = \mathbf{0}. \quad (10)$$

Because the direct RPA  $\mathbf{A}$  is positive definite,<sup>8</sup> the only solution is  $\mathbf{T} = \mathbf{0}$ . Thus the spin-flip components of  $\mathbf{T}$  vanish, and in the closed shell case all triplet components of  $\mathbf{T}$  vanish. Triplets do not contribute to direct RPA.

A third advantage of direct RPA is that the correlation energy expression is well defined, unlike in full RPA.<sup>1</sup> While in both direct and full RPA, we have  $\text{Tr}(\mathbf{BT}) = \text{Tr}(\boldsymbol{\omega} - \mathbf{A})$ ,<sup>8</sup> only in direct RPA is the prefactor in the correlation energy unambiguously 1/2. For full RPA, the plasmonic formula suggests the prefactor should be 1/2, while the connection to CC theory suggests that the prefactor should be 1/4. Moszynski *et al.*<sup>25</sup> presented another alternative full RPA energy expression that uses the plasmonic prefactor of 1/2 but subtracts the second-order MP2 correlation energy.

The elimination of exchange integrals in direct RPA may appear artificial from a wave function perspective, and in fact the wave function underlying direct RPA can violate the Pauli exclusion principle. However, direct RPA can be rigorously derived by applying the adiabatic connection fluctuation-dissipation theorem to the Kohn–Sham noninter-

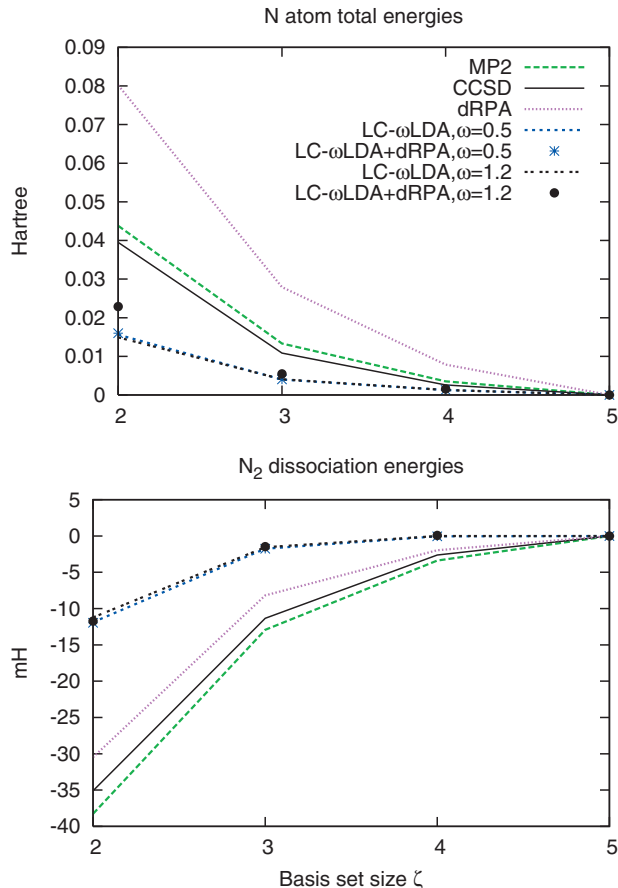


FIG. 1. (Color) Basis set dependence of LC- $\omega$ LDA+dRPA. (Top) Total energy of N atom. (Bottom) Dissociation energy of N<sub>2</sub> at experimental bond length 1.098 Å. Results are calculated with aug-cc-pV $\zeta$ Z basis sets and normalized to the aug-cc-pV5Z result. LC- $\omega$ LDA+dRPA calculations use  $c_{\text{RPA}} = 1$  and either  $\omega = 0.5$  or  $\omega = 1.2$  bohr<sup>-1</sup>.

acting reference system.<sup>3,5</sup> On balance, LR direct RPA from the GKS reference appears to be a practical ansatz for LR correlation.

### III. COMPUTATIONAL DETAILS

We have implemented our expressions into the development version of the GAUSSIAN suite of programs.<sup>26</sup> Matrices  $\mathbf{A}$  and  $\mathbf{B}$  are evaluated in the full spin-orbital basis set without symmetry adaptation. We use the range-separated LSDA correlation functional of Paziani *et al.*<sup>27</sup> In what follows, “LC- $\omega$ LDA” denotes GKS calculations using SR LSDA xc and LR HF exchange. (Note that in our previous papers, this acronym denoted SR LSDA exchange, LR HF exchange, and *full-range* LSDA correlation.) Adding LR direct RPA correlation as described above results in “LC- $\omega$ LDA+dRPA.” The “dRPA” acronym by itself denotes conventional, full-range (i.e., not range-separated) HF exchange and direct RPA correlation; this dRPA energy is evaluated from self-consistent Kohn–Sham orbitals and orbital energies calculated with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) xc functional.<sup>28</sup> Open shell systems are treated spin unrestricted. Equation (3) is solved iteratively using direct inversion in the iterative subspace (DIIS)<sup>29,30</sup> for coupled cluster. Correlated calculations use frozen core electrons.

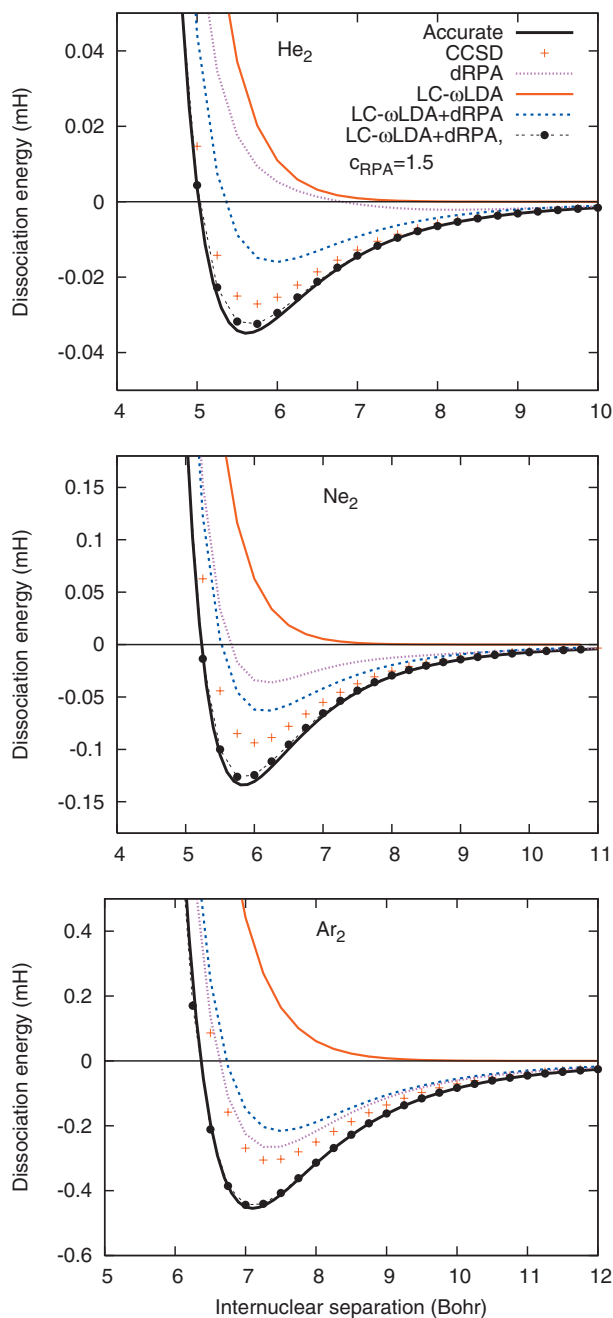


FIG. 2. (Color) Counterpoise-corrected dissociation curves of van der Waals dimers. aug-cc-pV5Z basis; other details in the text.

Like other workers,<sup>9–19</sup> we select the range separation parameter  $\omega$  empirically. Our standard LC- $\omega$ LDA+dRPA calculations set  $c_{\text{RPA}}=1$  in Eq. (6). We also explore treating  $c_{\text{RPA}}$  as an empirical parameter.

#### IV. NUMERICAL RESULTS

Figure 1 shows the basis set dependence of LC- $\omega$ LDA+dRPA for the total energy of N atom (top) and the dissociation energy of N<sub>2</sub> (bottom). As in previous work,<sup>17,20,32</sup> the LR correlation has a much weaker basis set dependence than full-range correlation. Calculations at the relatively large  $\omega=1.2$  bohr<sup>-1</sup>, which incorporate a larger fraction of direct RPA correlation, converge more slowly with basis set size.

TABLE I. Mean absolute errors (kcal/mol) in AE6 atomization energies, G2/97 heats of formation, BH6 and HTBH38/04 hydrogen-transfer reaction barrier heights, and NHTBH38/04 non-hydrogen-transfer barrier heights. 6-311+G(2d,2p) basis set.  $\omega$  in bohr<sup>-1</sup>.

Method	$\omega$	AE6	G2	BH6	HT	NHT
LC- $\omega$ PBE <sup>a</sup>	0.4	5.5	4.2	1.2	1.3	2.0
LC- $\omega$ LDA <sup>b</sup>	0.5	5.8	7.0	2.3	3.0	4.4
LC- $\omega$ LDA+dRPA	0.7	5.6	6.2	1.8	2.3	3.5
LC- $\omega$ LDA+dRPA <sup>c</sup>	1.2	4.0	4.4	1.2	1.6	3.5

<sup>a</sup>Reference 31.

<sup>b</sup>SR LSDA xc.

<sup>c</sup> $c_{\text{RPA}}=1.5$ .

Figure 2 shows counterpoise-corrected dissociation curves of van der Waals dimers He<sub>2</sub>, Ne<sub>2</sub>, and Ar<sub>2</sub>, evaluated in the large aug-cc-pV5Z basis set.<sup>33</sup> Accurate curves are from Ref. 34. LC- $\omega$ LDA and LC- $\omega$ LDA+dRPA use  $\omega=1.2$  bohr<sup>-1</sup>. Rescaling the LR dRPA correlation with  $c_{\text{RPA}}=1.5$  significantly improves the results, suggesting that the rescaling primarily corrects for beyond-dRPA correlation effects rather than basis set incompleteness. The weak He<sub>2</sub> binding of standard (full-range) dRPA is increased by using BP86 rather than PBE orbitals and orbital energies, consistent with Ref. 5 (not shown).

Table I shows mean absolute errors in the small AE6 and BH6 sets of 6 atomization energies and 6 reaction barrier heights,<sup>35</sup> the G2/97 set of 148 heats of formation<sup>36</sup> and the HTBH38/04 and NHTBH38/04 sets of 38 hydrogen-transfer and 38 non-hydrogen-transfer barrier heights.<sup>37,38</sup> Calculations use the 6-311+G(2d,2p) basis set. G2/97 calculations use B3LYP/6-31G(2df,p) geometries and vibrational frequencies,<sup>39</sup> other geometries and reference values are taken from Refs. 35–38. Results are presented for the thermochemically optimal  $\omega$ . LC- $\omega$ LDA+dRPA is quite accurate for thermochemistry and kinetics, particularly with the empirical rescaling  $c_{\text{RPA}}=1.5$ . It improves upon the underlying LC- $\omega$ LDA, giving results comparable to the accurate LC- $\omega$ PBE combination of range-separated GGA exchange and full-range GGA correlation.<sup>31</sup> Adding LR dRPA to LC- $\omega$ PBE appears to give significant double-counting of correlation (not shown). However, combining LR dRPA with a SR GGA (as in Ref. 20) may provide further improvements.

One of our goals is to apply range-separated dRPA to metallic systems. This is possible because dRPA is robust as the band gap closes. Figure 3 illustrates LC- $\omega$ LDA+dRPA in one such prototypical system. The figure plots the energy of spin- and symmetry-restricted aug-cc-pVTZ H<sub>2</sub> as a function of H–H bond length. The MP2 correlation energy diverges as the bond length increases and the HOMO-LUMO gap approaches zero. Full RPA (not shown) yields nonreal correlation energies for bonds stretched beyond the Coulson–Fischer point. In contrast, the LC- $\omega$ LDA+dRPA energy is real and finite at all bond lengths. LR dRPA does not capture all of the nondynamical correlation present in stretched symmetric singlet H<sub>2</sub>, and the dissociation limit is thus predicted too high in energy. The functional also overestimates the energy near equilibrium, especially with the empirical  $c_{\text{RPA}}$  rescaling. However, there is a definite improvement over both LC- $\omega$ LDA and MP2.

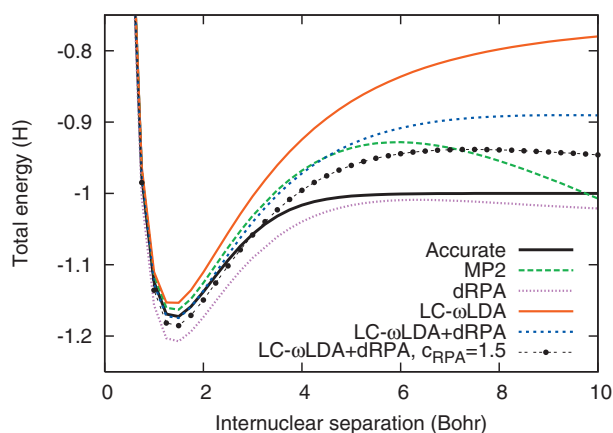


FIG. 3. (Color) Dissociation of symmetry-restricted singlet  $H_2$ . aug-cc-pVTZ basis set;  $\omega=1.2$  bohr $^{-1}$ . “Accurate” results are full CI/aug-cc-pV5Z.

The addition of LR RPA correlation to range-separated hybrid density functionals is a promising route to systematically incorporating nonlocal correlation effects into DFT. LC- $\omega$ LDA+dRPA can be evaluated in  $\mathcal{O}(N^4)$  time via Cholesky decomposition of  $\mathbf{A}$  and  $\mathbf{B}$ . It is robust to unstable and degenerate reference states and shows promise for systems from metals to covalent bonds to van der Waals complexes.

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