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Citation: *The Journal of Chemical Physics* **129**, 114105 (2008);

View online: <https://doi.org/10.1063/1.2977789>

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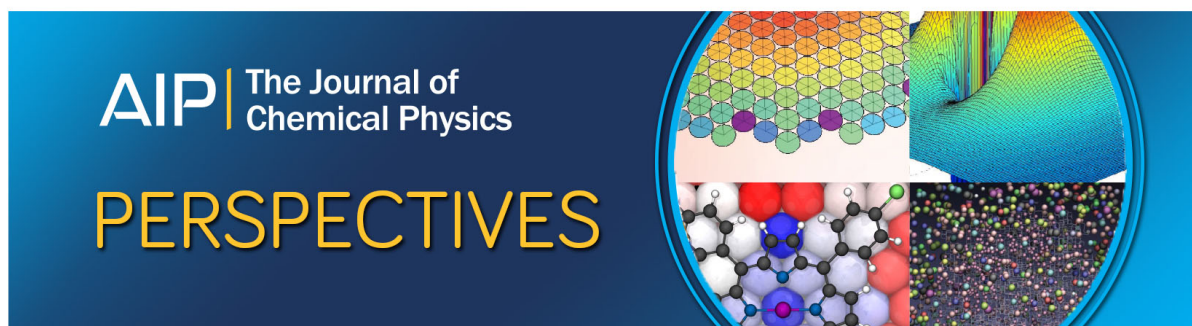
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Developing the random phase approximation into a practical post-Kohn–Sham correlation model

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(Received 14 July 2008; accepted 13 August 2008; published online 17 September 2008)

The random phase approximation (RPA) to the density functional correlation energy systematically improves upon many limitations of present semilocal functionals, but was considered too computationally expensive for widespread use in the past. Here a physically appealing reformulation of the RPA correlation model is developed that substantially reduces its computational complexity. The density functional RPA correlation energy is shown to equal one-half times the difference of all RPA electronic excitation energies computed at full and first order coupling. Thus, the RPA correlation energy may be considered as a difference of electronic zero point vibrational energies, where each eigenmode corresponds to an electronic excitation. This surprisingly simple result is intimately related to plasma theories of electron correlation. Differences to electron pair correlation models underlying popular correlated wave function methods are discussed. The RPA correlation energy is further transformed into an explicit functional of the Kohn–Sham orbitals. The only nontrivial ingredient to this functional is the sign function of the response operator. A stable iterative algorithm to evaluate this sign function based on the Newton–Schulz iteration is presented. Integral direct implementations scale as the fifth power of the system size, similar to second order Møller–Plesset calculations. With these improvements, RPA may become the long-sought robust and efficient zero order post-Kohn–Sham correlation model. © 2008 American Institute of Physics. [DOI: 10.1063/1.2977789]

I. INTRODUCTION

A well-established route to improved density functionals is to identify parts of the total electronic ground state energy functional suitable for approximation and treat the remainder exactly. Ground-breaking successes of this strategy were the Kohn–Sham (KS) method,¹ which treats the noninteracting kinetic energy exactly, and the more recent exact exchange methods including hybrid functionals.² At the next stage, part of the electron correlation energy must be computed exactly. Here the central problem is to identify a zero order treatment that captures the most important correlation effects, yet is efficient enough to be widely applicable in chemistry and solid state physics.

In single-reference post Hartree–Fock (HF) theory, the most popular zero order correlation treatment is second order Møller–Plesset perturbation theory (MP2). For single-reference ground states, MP2 energy differences are accurate to a few kcal/mol;³ the formal scaling of computational cost as the fifth power of the system size is manageable, and modern implementations are capable of applications in the 100 atoms regime. The density functional analog of MP2, second order Görling–Levy perturbation theory (GL2),⁴ is more sensitive than MP2 to near-degeneracy effects and severely overbinds multiply bonded molecules,⁵ despite its exactness in the high-density (low coupling strength) limit. This failure of GL2 has been a major obstacle to the development of correlated post-KS methods. An early remedy was

the interaction strength interpolation proposed by Seidl and Perdew,⁶ a Padé-type resummation of GL perturbation theory. A variant of GL perturbation theory using a different zero order Hamiltonian was introduced by Schweigert *et al.*⁷ To date, these methods have not found widespread use. Grimme recently proposed the Becke–Lee–Yang–Parr functional with second-order correlation (B2PLYP) functional, mixing the MP2 and generalized gradient approximation (GGA) energy functionals in a hybrid fashion.⁸ B2PLYP improves over conventional hybrid functionals for (mostly organic) thermochemistry, and a number of promising applications have been reported. For small gap systems, B2PLYP is bound to inherit the divergence of GL2 and MP2. B2PLYP yields an infinite correlation energy when applied to the uniform gas, which essentially precludes systematic improvement of the GGA part.

A strong candidate for a zero order post-KS correlation model is the random phase approximation (RPA) correlation energy. The RPA ground state energy functional is

$$E^{\text{RPA}} = T^{\text{S}} + V^{\text{ext}} + E^{\text{H}} + E^{\text{X}} + E^{\text{CRPA}}, \quad (1)$$

where T^{S} denotes the noninteracting kinetic energy, V^{ext} the external (nuclear) potential energy, E^{H} the Hartree energy, E^{X} the exact exchange energy, and E^{CRPA} the RPA correlation energy. Thus, as opposed to the GGA level, the exchange energy and part of the correlation energy are treated exactly in RPA. The origins of RPA go back to Bohm's and Pines's^{9,10} plasma theory of electron correlation in the early 1950s. The RPA correlation energy in a density functional

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context was defined by Langreth and Perdew in 1975.¹¹ In the following decades, Dobson¹² pioneered the theoretical development of RPA, and applied it to van der Waals interactions of extended systems. The first applications to molecules were published in 2001.¹³ Recent years have seen a steady growth of interest in the RPA, with implementations for molecules,^{14,15} atoms,^{16,17} and solids.¹⁸

The RPA model has a number of attractive features: First, RPA is not perturbative and corresponds to a partial resummation of the GL perturbation series. The RPA correlation energy is finite for metallic systems and for the uniform gas. At low coupling strength or high density, the RPA correlation energy reproduces the direct part of GL2 for any system. RPA is thus a stable generalization of GL2. Second, although total RPA correlation energies do not improve upon the GGA ones, correlation contributions to atomization energies are approximately three times more accurate at the RPA level compared to the GGA level.^{13,19} Since there is no need for error cancellation between approximate exchange and correlation within RPA, RPA calculations use the exact exchange energy functional. This dramatically reduces Coulomb self-interaction error, a central limitation of present-day semilocal functionals. Third, the RPA includes long-ranged van der Waals interactions in a “dispersion consistent” fashion, i.e., it yields molecular interaction energies at the *coupled* KS monomer level for large intermolecular separations.²⁰ In the uniform gas, the RPA covers the most-long-ranged part of the pair-distribution function. This suggests that correlation effects beyond RPA are short-ranged, and may be accurately approximated by semilocal functionals.²¹

The comparatively high computational cost is presently the most serious obstacle to further development of RPA correlation methods. My 2001 implementation¹³ scales as N^6 , where N measures the system size. Fuchs and Gonze¹⁴ claimed an $O(N^4)$ scaling for their method, but presented results for H_2 , He_2 , and Be_2 only. The slow basis set convergence convergence of RPA correlation energies¹³ is characteristic of methods that expand the electron coalescence cusp in a single-particle basis and adds to the computational complexity of RPA calculations. To become a viable zero order correlation model of practical and greater theoretical interest, the efficiency of molecular RPA correlation energy calculations must be substantially improved.

The present work introduces methods that reduce the cost of molecular RPA correlation energy calculations by several orders of magnitude, and improve upon the scaling. This is possible by a new, intuitively and computationally appealing formulation of the RPA correlation model. Exploiting the variational stability of RPA excitation energies along the lines of McLachlan and Ball,²² I will show in Sec. II that the RPA correlation energy functional is exactly given by the difference of correlated and uncorrelated electronic zero point vibrational energies (ZPVEs). The resulting expression is fully analytical and does not require any numerical frequency or coupling strength integration, which greatly simplifies the computations. An interpretation in the contexts of plasma theory and wave function theory is presented in Sec. III. In Sec. IV, I will introduce a method to compute the RPA

correlation energy without explicit evaluation of all excitation energies. This method involves computation of the sign function of the response operator as rate-determining step. I will outline an $O(N^5)$ scaling algorithm, and present first numerical examples. Conclusions are drawn in Sec. V.

II. THE PLASMON FORMULA

RPA belongs to the family of adiabatic connection fluctuation-dissipation theorem density functional methods.^{11,12,19} These methods use the zero-temperature fluctuation-dissipation theorem to express the ground state correlation energy functional in terms of the imaginary (dissipative) part of the frequency-dependent density-density response function $\chi_\alpha(\omega, x_1, x_2)$

$$E^C = -\frac{1}{2} \text{Im} \int_0^1 d\alpha \int_0^\infty \frac{d\omega}{\pi} \int dx_1 dx_2 \times \frac{\chi_\alpha(\omega, x_1, x_2) - \chi_0(\omega, x_1, x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2)$$

where x denotes spin and space coordinates of an electron. At every electron interaction strength α , the external potential is chosen to constrain the ground state density to equal the physical ($\alpha=1$) ground state density. Thus, $\alpha=0$ corresponds to the noninteracting KS system, while the full interacting system is recovered at $\alpha=1$.

Time-dependent density functional theory (TDDFT) has shown²³ that $\chi_\alpha(\omega, x_1, x_2)$ satisfies the Dyson equation

$$\chi_\alpha(\omega, x_1, x_2) = \chi_0(\omega, x_1, x_2) + \int dx'_1 dx'_2 \chi_0(\omega, x_1, x'_1) \times f_\alpha^{\text{HXC}}(\omega, x'_1, x'_2) \chi_\alpha(\omega, x'_2, x_2). \quad (3)$$

Equations (2) and (3) are exact, but involve the frequency-dependent Hartree, exchange and correlation kernel $f_\alpha^{\text{HXC}}(\omega, x_1, x_2)$, which is unknown as an explicit density functional. The RPA ignores exchange and correlation effects in $f_\alpha^{\text{HXC}}(\omega, x_1, x_2)$ and replaces it by the Hartree kernel, $\alpha/|\mathbf{r}_1 - \mathbf{r}_2|$. Thus, the RPA version of Eq. (3) is

$$\chi_\alpha^{\text{RPA}}(\omega, x_1, x_2) = \chi_0(\omega, x_1, x_2) + \alpha \int dx'_1 dx'_2 \frac{\chi_0(\omega, x_1, x'_1) \chi_\alpha^{\text{RPA}}(\omega, x'_2, x_2)}{|\mathbf{r}'_1 - \mathbf{r}'_2|}, \quad (4)$$

which can be solved for χ_α^{RPA} . The use of the latter in Eq. (2) defines the RPA correlation energy, E^{CRPA} .

Straightforward evaluation of Eq. (2) is impractical because it involves, apart from an integration over two electron coordinates, integrations over the coupling strength α and the frequency ω . It was generally believed that, if the coupling strength integration is performed using Eq. (4), the frequency integration has to be performed numerically. It is reasonable to assume that constant accuracy in E^{CRPA} requires ω grids growing superlinearly with N , because the number of poles in χ_α^{RPA} grows as $O(N^2)$ [see Eq. (5) below]. For similar reasons, a strong dependence of the ω grid size to the basis

set and inclusion or omission of core excitations must be expected, making numerical ω integration unattractive.

The frequency dependence of χ_α^{RPA} is obvious from its spectral or Lehmann representation,

$$\chi_\alpha^{\text{RPA}}(\omega, x_1, x_2) = - \sum_n \left(\frac{\rho_{an}(x_1)\rho_{an}(x_2)}{\Omega_{an} - \omega - i\eta} + \frac{\rho_{an}(x_1)\rho_{an}(x_2)}{\Omega_{an} + \omega + i\eta} \right), \quad (5)$$

where $\Omega_{an}, \rho_{an}(x)$ are RPA excitation energies and transition densities at coupling strength α , and $i\eta$ is a small contour distortion making χ_α^{RPA} analytical in the upper complex plane. Using $\text{Im} \frac{1}{\omega+i\eta} = -\pi\delta(\omega)$, the ω integration in Eq. (2) becomes trivial, yielding

$$E^{\text{CRPA}} = \frac{1}{2} \int_0^1 d\alpha \sum_n \int dx_1 dx_2 \times \frac{\rho_{an}(x_1)\rho_{an}(x_2) - \rho_{0n}(x_1)\rho_{0n}(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (6)$$

Thus, E^{CRPA} equals the coupling strength average over the Hartree energy differences of all transition densities. The latter are conveniently expanded in a basis of static KS spin orbital products,²⁴

$$\rho_{an}(x) = \sum_{ia} (X_{an} + Y_{an})_{ia} \phi_i(x) \phi_a(x), \quad (7)$$

where indices i, j, \dots indicate occupied and indices a, b, \dots virtual ground state KS molecular orbitals (MOs), and all MOs are chosen real. The vectors

$$\begin{pmatrix} X_{an} \\ Y_{an} \end{pmatrix} = |X_{an}, Y_{an}\rangle \quad (8)$$

and the excitation energies $\Omega_{an} > 0$ are solutions of the non-Hermitian eigenvalue problem

$$(\Lambda_\alpha - \Omega_{an}\Delta)|X_{an}, Y_{an}\rangle = 0 \quad (9a)$$

under the orthonormality constraint

$$\langle X_{am}, Y_{am} | \Delta | X_{an}, Y_{an} \rangle = \delta_{mn}. \quad (9b)$$

The operators (sometimes called superoperators)

$$\Lambda_\alpha = \begin{pmatrix} A_\alpha & B_\alpha \\ B_\alpha & A_\alpha \end{pmatrix}, \quad \Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (10)$$

contain the RPA version of the so-called orbital rotation Hessians,¹³

$$(A_\alpha + B_\alpha)_{iajb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + 2\alpha \langle ij|ab \rangle, \quad (11)$$

$$(A_\alpha - B_\alpha)_{iajb} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab},$$

where $\langle ij|ab \rangle$ is an electron repulsion integral in the Dirac notation and $\epsilon_a - \epsilon_i$ are zero order KS orbital energy differences. Equations (9a) and (9b) generalize²⁴ the Dyson Equation (3) and are widely used to compute excitation energies and transition properties in time-dependent Hartree-Fock (TDHF) and TDDFT.^{22,25,26}

The largest RPA correlation energy calculations reported for molecules so far^{13,19} effectively evaluated Eq. (6) by computing all transition densities $\rho_{an}(x)$ from Eqs. (7), (9a), and (9b) followed by numerical coupling strength integration. The latter is less critical than numerical frequency integration, but complete diagonalization of $\Lambda_\alpha - \Omega\Delta$ at each α integration point scales as N^6 with a large prefactor.

I will now show that both the frequency and the coupling strength integrations may be performed analytically. Because of Eqs. (9a) and (9b), the excitation energy

$$\Omega_{an} = \langle X_{an}, Y_{an} | \Lambda_\alpha | X_{an}, Y_{an} \rangle \quad (12)$$

is stationary with respect to first order variations of $|X_{an}, Y_{an}\rangle$. Thus, the Hellmann-Feynman theorem holds and

$$\frac{d\Omega_{an}}{d\alpha} = \langle X_{an}, Y_{an} | \frac{d\Lambda_\alpha}{d\alpha} | X_{an}, Y_{an} \rangle. \quad (13)$$

Using Eqs. (10) and (11), the first order response operator is, within RPA,

$$\frac{d\Lambda_\alpha}{d\alpha} = \Lambda^{(1)} = \begin{pmatrix} C & C \\ C & C \end{pmatrix}, \quad (14)$$

where $C_{iajb} = \langle ij|ab \rangle$. Thus,

$$\begin{aligned} \frac{d\Omega_{an}}{d\alpha} &= \sum_{iajb} (X_{an} + Y_{an})_{ia} \langle ij|ab \rangle (X_{an} + Y_{an})_{jb} \\ &= \int dx_1 dx_2 \frac{\rho_{an}(x_1)\rho_{an}(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \end{aligned} \quad (15)$$

i.e., the coupling strength derivative of Ω_{an} equals twice the Hartree energy of the transition density within RPA. Using this result, Eq. (6) becomes

$$E^{\text{CRPA}} = \frac{1}{2} \int_0^1 d\alpha \sum_n \left(\frac{d\Omega_{an}}{d\alpha} - \left. \frac{d\Omega_{an}}{d\alpha} \right|_{\alpha=0} \right). \quad (16)$$

This is easily integrated over coupling strength to yield a central result of the present paper,

$$E^{\text{CRPA}} = \frac{1}{2} \sum_n (\Omega_n - \Omega_n^{\text{D}}). \quad (17)$$

Ω_n is the n th RPA excitation energy at full coupling, and Ω_n^{D} is the sum of the zero and first order RPA excitation energies,

$$\Omega_n^{\text{D}} = \Omega_{0n} + \left. \frac{d\Omega_{an}}{d\alpha} \right|_{\alpha=0}. \quad (18)$$

The Ω_n^{D} equal the eigenvalues of $\Lambda - \Omega\Delta$ if all off-diagonal elements of $(A+B)$ (in the KS orbital basis) are neglected; this is closely related to the single pole approximation in TDDFT.²³ If the excitation n reduces to the single-particle transition $i \rightarrow a$ in the zero coupling ($\alpha=0$) limit,

$$\Omega_n^{\text{D}} = \epsilon_a - \epsilon_i + \langle ii|aa \rangle, \quad (19)$$

compare Sec. III B.

III. PHYSICAL INTERPRETATION OF THE RPA CORRELATION MODEL

A. Plasmon picture

According to Eq. (17), the RPA correlation energy may be viewed as the difference of electronic ZPVEs

$$\text{ZPVE}_\alpha = \frac{1}{2} \sum_n \Omega_{an} \quad (20)$$

at full coupling and to first order in α . In this picture, each electronic eigenmode $|X_{an}, Y_{an}\rangle$ corresponds to one harmonic oscillator with angular frequency Ω_{an} . As the coupling strength α increases, the $|X_{an}, Y_{an}\rangle$ change from single-particle excitations of the KS system into collective density modes (within RPA). The RPA correlation energy measures the change in the ground state energy of these collective density modes due to electron interactions. In the uniform electron gas, the index n is replaced by the wavevector \mathbf{q} denoting the momentum transfer upon excitation. The long wavelength ($q \rightarrow 0$) limit of $\Omega_{\mathbf{q}}$ is the classical plasmon frequency.²⁷

To first order, the ZPVE equals $\frac{1}{2}\text{tr}(A)$, because

$$\text{ZPVE}^D = \frac{1}{2} \sum_n \Omega_n^D = \frac{1}{2} \sum_{ia} (\epsilon_a - \epsilon_i + \langle ii|aa \rangle) = \frac{1}{2} \text{tr}(A). \quad (21)$$

The eigenvalues of A , Ω_n^{TDA} , correspond to the Tamm-Dancoff approximation²⁷ to the RPA excitation energies at full coupling. Since the trace is a unitary invariant, Eq. (21) may be rewritten

$$\text{ZPVE}^D = \frac{1}{2} \sum_n \Omega_n^{\text{TDA}} = \text{ZPVE}^{\text{TDA}}, \quad (22)$$

and by Eq. (17), an alternative expression for the RPA correlation energy is

$$E^{\text{CRPA}} = \frac{1}{2} \sum_n (\Omega_n - \Omega_n^{\text{TDA}}). \quad (23)$$

The TDA is equivalent to constraining the variation of all RPA excitation energies, Eq. (12), to the space of positive energy single-particle excitation by setting $Y=0$. Since this is a linear constraint, McDonald's theorem applies and²⁸

$$\Omega_n \leq \Omega_n^{\text{TDA}}. \quad (24)$$

Thus, the RPA correlation energy is always nonpositive. While the TDA has successfully been used in excitation energy calculations, it is invalid here, yielding zero correlation energies when used to approximate the full RPA excitation energies. It is the mixing of positive and negative energy excitations caused by the B matrix and reflected by $Y \neq 0$ that gives rise to electron correlations in the RPA.

The simple and appealing physical picture underlying RPA goes back to the plasma theory of electron correlation. This theory, first proposed by Bohm and Pines^{9,10} in 1952 and later refined by Nozières and Pines,²⁹ produced the first quantitative correlation energies for the uniform electron gas. Bohm and Pines suggested to transform the interacting uni-

form gas Hamiltonian to a sum of decoupled harmonic oscillator Hamiltonians, whose ZPVE covers the long-range part of the ground state correlation energy. This was achieved by a series of approximations. One of these approximations consists in an assumed cancellation of phases of collective density modes, giving rise to the name "random phase approximation." Equation (17) does not appear in this early work, and neither the results of Bohm and Pines nor the Pines-Nozières treatment are fully equivalent to the RPA defined by Eqs. (2) and (4).

A HF version of Eq. (17) appeared in McLachlan's and Ball's²² ground-breaking 1964 paper on TDHF theory; it differs from Eq. (17) by a factor of 1/2. While the TDHF RPA was widely used to compute molecular response properties, few results for ground state correlation energies were reported^{28,30} (for a review of TDHF RPA correlation energy calculations see Ref. 31). Despite some theoretical development,³²⁻³⁴ McLachlan's and Ball's formula appears to have been largely ignored after 1980, possibly due to triplet instabilities that affect the TDHF RPA (Ref. 31) but not the present formalism, because all triplet excitation energies cancel out of Eq. (17). To the best of my knowledge, it has never clearly been recognized that Eq. (17) yields the exact density functional RPA correlation energy for any system.

B. Wave function picture

Equation (17) may be recast to bring out more clearly the relation to correlated wave function theories. For $\alpha \rightarrow 0$, each eigenvector $|X_{an}, Y_{an}\rangle$ reduces to some vector $|X_{ia}^{(0)}, Y_{ia}^{(0)}\rangle$, with $X_{ia}^{(0)} = \delta_{ia}$, $Y_{ia} = 0$. This is a single-particle excitation of the noninteracting KS system. The corresponding excitation energy goes to $\Omega_{ia}^{(0)} = \epsilon_a - \epsilon_i$, i.e., the bare KS orbital energy difference. Because at finite α the noncrossing theorem for the eigenvalues Ω_{an} holds, each n may be uniquely assigned, up to zero order degeneracies, to a noninteracting transition $i \rightarrow a$. This holds as long as the response operator Λ is frequency independent, which is satisfied in the RPA. Choosing intermediate normalization, the eigenvector at full coupling belonging to ia may be decomposed into a KS zero order part and a correlation part,

$$|X_n, Y_n\rangle = |X_{ia}^{(0)}, Y_{ia}^{(0)}\rangle + |X_{ia}^C, Y_{ia}^C\rangle, \quad (25)$$

where normalization is now chosen such that

$$\langle X_{ia}^{(0)}, Y_{ia}^{(0)} | \Delta | X_{ia}^C, Y_{ia}^C \rangle = 0. \quad (26)$$

Thus, $|X_{ia}^C, Y_{ia}^C\rangle$ may be expanded in the basis of KS excitations of positive and negative energy,

$$|X_{ia}^C, Y_{ia}^C\rangle = \sum_{jb} (X_{iajb}^C |X_{jb}^{(0)}, Y_{jb}^{(0)}\rangle + Y_{iajb}^C |Y_{jb}^{(0)}, X_{jb}^{(0)}\rangle), \quad (27)$$

with $X_{iaia}^C = Y_{iaia}^C = 0$ by Eq. (26).

Requiring $|X_n, Y_n\rangle$ to satisfy eigenvalue problem (9a), we obtain a standard result for the eigenvalue,

$$\begin{aligned}\Omega_n = \Omega_{ia} &= \Omega_{ia}^{(0)} + \Omega_{ia}^{(1)} + \langle X_{ia}^{(0)}, Y_{ia}^{(0)} | \Lambda^{(1)} | X_{ia}^C, Y_{ia}^C \rangle \\ &= \Omega_{ia}^D + \sum_{jb} \langle ij|ab \rangle (X + Y)_{iajb}^C.\end{aligned}\quad (28)$$

The collective part $|X_{ia}^C, Y_{ia}^C\rangle$ satisfies the coupled equation system

$$(\epsilon_b - \epsilon_j - \Omega_{ia}) X_{iajb}^C + \sum_{kc} \langle jk|bc \rangle (X + Y)_{iakc}^C = -\langle ij|ab \rangle, \quad (29a)$$

$$(\epsilon_b - \epsilon_j + \Omega_{ia}) Y_{iajb}^C + \sum_{kc} \langle jk|bc \rangle (X + Y)_{iakc}^C = -\langle ij|ab \rangle. \quad (29b)$$

Equations (29a) and (29b) are nonlinear, because the excitation energies Ω_{ia} are a functional of $|X_{ia}^C, Y_{ia}^C\rangle$ by Eq. (28). Inserting the eigenvalues into the plasmon formula, Eq. (17), a simple result for the RPA correlation energy follows,

$$E^{\text{CRPA}} = \frac{1}{2} \sum_{iajb} \langle ij|ab \rangle (X + Y)_{iajb}^C. \quad (30)$$

A connection to correlated wave function theory is established through the relation

$$\begin{aligned}E^C &= \langle \Phi | H - H^{\text{KS}} | \Psi^C \rangle \\ &= \sum_{ia} \langle \Phi | V^{\text{ee}} - V^{\text{HXC}} | \Phi_i^a \rangle t_i^a + \frac{1}{4} \sum_{iajb} \langle \Phi | V^{\text{ee}} | \Phi_{ij}^{ab} \rangle t_{ij}^{ab}, \\ &= \sum_{ia} \langle \Phi | V^{\text{ee}} - V^{\text{HXC}} | \Phi_i^a \rangle t_i^a + \frac{1}{2} \sum_{iajb} \langle ij|ab \rangle t_{ij}^{ab},\end{aligned}\quad (31)$$

which is a consequence of the Schrödinger equation for the interacting ground state $|\Psi\rangle$. H and H^{KS} are the interacting and KS Hamiltonians, V^{ee} denotes the full electron interaction, and V^{HXC} the sum of the Hartree, exchange, and correlation potential operators; $|\Phi\rangle$ is KS ground state determinant, and $|\Phi_i^a\rangle$ and $|\Phi_{ij}^{ab}\rangle$ denote singly and doubly excited KS determinants, respectively. The interacting wave function $|\Psi\rangle$ in intermediate normalization has the expansion

$$|\Psi\rangle = |\Phi\rangle + |\Psi^C\rangle = |\Phi\rangle + \sum_{ia} t_i^a |\Phi_i^a\rangle + \frac{1}{4} \sum_{iajb} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \dots \quad (32)$$

In contrast to the textbook expression for the ground state HF correlation energy,³⁵ the density functional correlation energy, Eq. (31) involves singles excitations, too, because Brillouin's theorem does not hold in the KS case.

Comparing Eqs. (30) and (31), it follows that RPA corresponds to setting

$$t_i^a = 0, \quad t_{ij}^{ab} = (X + Y)_{iajb}^C. \quad (33)$$

Thus, the RPA approximates the doubles amplitudes t_{ij}^{ab} by the collective part of the single excitation $|X_{ia}, Y_{ia}\rangle$. Analysis of TDHF one-electron transition properties starting from the hypervirial theorem leads to similar conclusions.³⁶ Although $t_{ii}^{aa} = 0$, the t_{ij}^{ab} in Eq. (33) are not antisymmetric under permutations of i and j or a and b ; this violation of Pauli's

principle reflects the neglect of exchange effects in the present bare RPA formalism. Equations (30), (29a), and (29b) also permit a comparison to well-established correlated wave function methods that approximate doubles amplitudes, such as pair correlation and coupled cluster theories.³⁵ A striking difference to pair theories is that the RPA correlation energy is a sum of *excitation* rather than *pair interaction* energy differences; likewise, the energy shift Ω_{ia} in Eqs. (29a) and (29b) is an excitation energy, not a pair energy. Another striking difference is the occurrence of a second set of coefficients, $(X - Y)_{iajb}^C$, in Eqs. (29a) and (29b), caused by the negative energy part of $|X_{ia}, Y_{ia}\rangle$. Equations (29a) and (29b) also differ qualitatively from the ‘‘ring approximation’’ to coupled cluster doubles theory, which has been applied to the uniform electron gas.³⁷ This is obvious, e.g., from the fact that TDA is a useful approximation to the latter,³⁸ while it entirely misses the point in the present approach, as discussed in Sec. III A.

IV. EFFICIENT COMPUTATION OF E^{CRPA}

The plasmon formula, Eq. (17), requires neither frequency nor coupling strength integration, which speeds up RPA correlation energy calculations by roughly an order of magnitude compared to previous implementations. The cost of a straightforward evaluation of Eq. (17) still grows as N^6 , because the complete spectrum of eigenvalues Ω_n must be computed. At first sight, iteration of Eqs. (30), (29a), and (29b) may seem a promising alternative, but closer inspection shows that it is difficult to implement the orthonormality constraint (9b) in this approach.

Equation (17) expresses E^{CRPA} in the special basis of $\Lambda_\alpha - \Omega\Delta$ eigenvectors at full and zero coupling. I will show in the following that Eq. (17) may be generalized to an arbitrary basis, making explicit computation of the eigenvalue spectrum Ω_n unnecessary. The idea is to compute E^{CRPA} from the trace of some not necessarily diagonal operator. As a first step, consider

$$\Delta\Lambda = \begin{pmatrix} A & B \\ -B & -A \end{pmatrix}. \quad (34)$$

Although $\Delta\Lambda$ is not self-adjoint, it has real eigenvalues $\pm\Omega_n$. This follows from Eq. (9a) using $\Delta^2 = 1$,

$$\Delta\Lambda |X_n, Y_n\rangle = \Omega_n |X_n, Y_n\rangle, \quad (35a)$$

$$\Delta\Lambda |Y_n, X_n\rangle = -\Omega_n |Y_n, X_n\rangle. \quad (35b)$$

$\Delta\Lambda$ is diagonalized by the similarity transformation

$$Z^{-1} \Delta\Lambda Z = \begin{pmatrix} \text{diag}(\Omega) & 0 \\ 0 & -\text{diag}(\Omega) \end{pmatrix}, \quad (36)$$

where Z and Z^{-1} may be expressed in terms of the eigenvectors at full and zero coupling,

$$Z = \sum_n (|X_n, Y_n\rangle\langle X_n^{(0)}, -Y_n^{(0)}| + |Y_n, X_n\rangle\langle Y_n^{(0)}, -X_n^{(0)}|), \quad (37a)$$

$$Z^{-1} = \sum_n (|X_n^{(0)}, Y_n^{(0)}\rangle\langle X_n, -Y_n| + |Y_n^{(0)}, X_n^{(0)}\rangle\langle Y_n, -X_n|). \quad (37b)$$

This follows from Eqs. (35a) and (35b) and the extended orthonormality relations

$$\langle X_m, Y_m | \Delta | X_n, Y_n \rangle = - \langle Y_m, X_m | \Delta | Y_n, X_n \rangle = \delta_{mn} \quad (38)$$

$$\langle X_m, Y_m | \Delta | X_n, Y_n \rangle = 0.$$

Equation (36) implies that $Z^{-1}\Delta\Lambda Z$ is a Jordan canonical form of $\Delta\Lambda$, with 1×1 Jordan blocks containing the eigenvalues.

E^{CRPA} cannot be computed from $\text{tr}(\Delta\Lambda)$, since, by Eq. (36),

$$\text{tr}(\Delta\Lambda) = \text{tr}(Z^{-1}\Delta\Lambda Z) = \sum_n (\Omega_n - \Omega_n) = 0. \quad (39)$$

If an operator S that changes the sign of the negative eigenvalues such that

$$Z^{-1}\Delta\Lambda SZ = \begin{pmatrix} \text{diag}(\Omega) & 0 \\ 0 & \text{diag}(\Omega) \end{pmatrix} \quad (40)$$

can be found, E^{CRPA} may be computed from $\text{tr}(\Delta\Lambda S)$. S is readily constructed using Eq. (36),

$$S = Z \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} Z^{-1} = Z\Delta Z^{-1}. \quad (41)$$

It turns out that this is the definition of the sign function³⁹ of $\Delta\Lambda$, i.e.,

$$S = \text{sign}(\Delta\Lambda). \quad (42)$$

Only the difference between the sign functions at full and zero coupling

$$\Sigma = \text{sign}(\Delta\Lambda) - \text{sign}(\Delta\Lambda^{(0)}) = \text{sign}(\Delta\Lambda) - \Delta, \quad (43)$$

enters the final expression for for E^{CRPA} ,

$$E^{\text{CRPA}} = \frac{1}{4} \text{tr}(\Delta\Lambda\Sigma). \quad (44)$$

Equation (44) is the essence of the present paper. It is the desired generalization of the plasmon formula, Eq. (17), to an arbitrary basis. Equation (44) is a rare example of a non-perturbative correlation energy that is an explicit functional of noninteracting quantities: All that is needed to evaluate Eq. (44) are the RPA response operators Λ and Δ , expressed in any basis. The most obvious choice is the basis of static KS orbitals, because Λ and Δ may be set up with $O(N^5)$ operations using Eqs. (10) and (11). $\text{Sign}(\Delta\Lambda)$ may be computed without prior diagonalization of $\Delta\Lambda$. The matrix sign function has been the subject of intense research due to its importance for the algebraic Riccati equations, e.g., in optimal control theory; an extensive literature including theoretical results and algorithms exists.^{39,40} In electronic structure theory, Németh and Scuseria⁴¹ used the matrix sign function to devise an efficient linear scaling algorithm for computing

TABLE I. Performance of the Newton–Schulz iteration for computing $\text{sign}(\Delta\Lambda)$. d is the dimension of particle-hole vector space of the specified irreducible representation of the molecular point group, κ denotes the condition number, and N_{it} the number of iterations required for $r < 10^{-10}$, where the residual norm r is defined in the Appendix. ΔE^{CRPA} denotes the difference in the correlation energies in Hartrees computed from Eq. (44) using the Newton–Schulz iteration and Eq. (17) using diagonalization. The PBE GGA (Ref. 43) and cc-pVQZ (Refs. 44 and 45) basis sets were used to compute the KS ground state structure and KS orbitals (Ref. 46). Very fine grids [size 5 (Ref. 58)] were used in the PBE calculations.

	O ₃ , B ₁	PH ₃ , E	C ₆ H ₆ , E _{2g}
d	526	418	1025
$\kappa(\Delta\Lambda)$	287	314	114
N_{it}	19	19	16
ΔE^{CRPA}	-1×10^{-12}	6×10^{-12}	-4×10^{-12}

the noninteracting one-particle density matrix avoiding diagonalization. Particularly appealing for the present purpose are methods that approximate $\text{sign}(\Delta\Lambda)$ by a finite-order polynomial of $\Delta\Lambda$. A straightforward method to generate such a polynomial approximation is the Newton–Schulz iteration for the matrix sign function:^{39,42} Starting from $S_0 = \Delta\Lambda$,

$$S_{k+1} = \frac{1}{2} S_k (3 \cdot \mathbf{1} - S_k^2) \quad (45)$$

converges quadratically to $\text{sign}(\Delta\Lambda)$ after S_0 has been appropriately scaled. The scaling procedure and further details of the implementation are described in the Appendix. Table I shows for three representative examples that the Newton–Schulz iteration for $\Delta\Lambda$ yields accurate RPA correlation energies and converges reasonably fast. The number of iterations increases slowly with the condition number $\kappa(\Delta\Lambda)$, which depends on the basis set size. The quadruple zeta valence basis sets used here yield reasonably accurate energy differences in molecular applications.¹³ The present explorative calculations were based on my 2001 implementation¹³ in TURBOMOLE.^{47,48}

It is of great practical significance that there are efficient and stable polynomial approximations to $\text{sign}(\Delta\Lambda)$. As detailed in the Appendix, any polynomial of $(\Delta\Lambda)^k$ may be re-expressed by mixed polynomials of $(A+B)$ and $(A-B)$ up to order k . If P denotes a $(k-1)$ th order polynomial, the only nontrivial operation is the multiplication of P by the off-diagonal part of $(A+B)$,

$$Q_{iajb} = 2 \sum_{kc} \langle jk|bc \rangle P_{iajb}. \quad (46)$$

Such matrix products may be evaluated with $O(N^5)$ operations if integral direct methods are used, i.e., if $\langle jk|bc \rangle$ is evaluated “on the fly” in the atomic orbital basis. This is a standard technique widely used in configuration interaction^{49,50} and coupled cluster theory.⁵¹ Thus, $(\Delta\Lambda)^k$ may be recursively computed at $O(N^5)$ computational cost starting from $P=1$. [Equation (44) could even be evaluated entirely in the atomic orbital basis set. This would further reduce the scaling with N , but increase the prefactor.]

At first sight, it may seem promising to evaluate E^{CRPA} from the trace of the symmetric matrix

$$M^{1/2} = [(A - B)^{1/2}(A + B)(A - B)^{1/2}]^{1/2}, \quad (47)$$

whose eigenvalues are all positive Ω_n .¹³ There are reasons to prefer Eq. (44): (i) Most useful iterative methods to compute matrix square roots are based on rewriting the problem in terms of the matrix sign function.⁵² (ii) $\kappa(M) = \kappa(\Delta\Lambda)^2$, so Eq. (44) is numerically advantageous. (iii) For nondiagonal $(A - B)$, it is impractical to compute M , while the use of Eq. (44) is straightforward. Likewise, it is possible to express E^{CRPA} in terms of the so-called sign factor

$$N = \Delta\Lambda \text{sign}(\Delta\Lambda) = [(\Delta\Lambda)^2]^{1/2} \quad (48)$$

generalizing the modulus of a real number. However, the most common methods to compute N use the sign function.³⁹ Another advantage of Eq. (44) is that once Σ has been computed, first order properties such as gradients with respect to nuclear positions or dipole moments are readily obtained from

$$E^{\text{CRPA}\xi} = \frac{1}{4} \text{tr}(\Delta\Lambda^\xi \Sigma), \quad (49)$$

where the superscript ξ denotes the first order derivative with respect to the perturbation. This is another consequence of the Hellmann–Feynman theorem [Eq. (13)].

V. CONCLUSIONS

There are two main results of the present work. First, the RPA correlation energy functional is simply the difference of RPA and first order electronic ZPVEs. Although similar results have been in the literature for a long time, it was not generally recognized that the plasmon formula, Eq. (17), exactly holds for any system. The second main result is that the plasmon formula may be recast into an explicit functional of the RPA response operator. The resulting expression, Eq. (44), is also a functional of the KS orbitals and contains the sign function of the response operator at full coupling. Stable polynomial approximations to the latter are available and may be implemented at $O(N^5)$ computational cost.

The methods developed here achieve a dramatic reduction of computational complexity in molecular RPA correlation energy calculations. The results of Sec. IV indicate that $O(N^5)$ implementations requiring little more effort than MP2 are within reach. Resolution of the identity (RI) methods⁵³ are straightforward to apply to RPA and hold promise of further substantial savings.

The present results also reveal simple and appealing physics underlying the RPA. That the RPA correlation energy is a difference of electronic ZPVEs is highly intuitive; this is by itself an argument to use it. There are plenty of directions to improve upon RPA. Examples are GGAs for short-range correlation,²¹ and perturbative or local field corrections to χ_α^{RPA} starting from Eq. (3), e.g., along the lines of Ref. 19 or the recently proposed inhomogeneous Singwi–Tosi–Land–Sjölander method.^{54,55} Connections to correlated wave function methods may be worth pursuing from either side, starting from, e.g., the results of Sec. III B. Almost all RPA correlation energy calculations reported so far (including the present ones) are post-KS and make use of GGA or exchange-only ground state densities and potentials. RPA correlation potentials are accessible via Green's function

techniques;^{56,57} recent results for atoms¹⁷ are promising, suggesting that self-consistent RPA calculations for larger systems will be possible. RPA has the potential to become a building block of future generations of electronic structure methods.

ACKNOWLEDGMENTS

I would like to thank K. Burke and T. Van Voorhis for discussions and R. Ahlrichs, J. G. Ángyán, A. Savin, G. E. Scuseria, and W. Yang for helpful comments. UCI start-up funds are gratefully acknowledged.

APPENDIX: ITERATIVE COMPUTATION OF E^{CRPA}

Applying the unitary transformation

$$U = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \quad (A1)$$

to Δ and Λ , Eq. (44) becomes

$$E^{\text{CRPA}} = \frac{1}{4} \text{tr}[(A + B)(K - 1) + (A - B)(L - 1)], \quad (A2)$$

where K and L are determined by

$$\begin{pmatrix} 0 & K \\ L & 0 \end{pmatrix} = \text{sign} \begin{pmatrix} 0 & (A - B) \\ (A + B) & 0 \end{pmatrix}. \quad (A3)$$

Thus, only two instead of four matrices need to be iterated and it can be used that $(A - B)$ is diagonal in the KS orbital basis. Before applying the Newton–Schulz iteration, (45), it is necessary to scale $(A + B)$ and $(A - B)$ by $\alpha, \beta > 0$,

$$(\tilde{A} + \tilde{B}) = \alpha(A + B), \quad (A4)$$

$$(\tilde{A} - \tilde{B}) = \beta(A - B).$$

The iteration is guaranteed to converge if all eigenvalues of $(\tilde{A} + \tilde{B})$ and $(\tilde{A} - \tilde{B})$ are less than 1.³⁹ Bounds for the largest eigenvalue of $(\tilde{A} + \tilde{B})$ can be computed iteratively or from Gershgorin's circle theorem.⁴¹ In practice, the simple choice (cf. Ref. 52)

$$\alpha = 1/\max_{ia} (A + B)_{iaia}, \quad (A5)$$

$$\beta = 1/\max_{ia} (A - B)_{iaia},$$

was found to yield quadratic convergence of the Newton–Schulz iteration for

$$\begin{pmatrix} 0 & \tilde{K} \\ \tilde{L} & 0 \end{pmatrix} = \text{sign} \begin{pmatrix} 0 & (\tilde{A} - \tilde{B}) \\ (\tilde{A} + \tilde{B}) & 0 \end{pmatrix} \quad (A6)$$

in all cases tested. The Euclidean norm $r = \|1 - \tilde{K}\tilde{L}\|$ was used as convergence indicator. After convergence, the unscaled quantities are recovered from

$$K = \sqrt{\frac{\beta}{\alpha}} \tilde{K},$$

$$L = \sqrt{\frac{\alpha}{\beta}} \tilde{L}. \tag{A7}$$

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