Fast computation of molecular RPA correlation energies using resolution-of-the-identity and imaginary frequency integration

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Abstract

The random phase approximation (RPA) is an increasingly popular method to compute post-Kohn-Sham correlation energies, but its high computational cost has limited molecular applications to systems with few atoms so far. Here we present an efficient implementation of RPA correlation energies based on a combination of resolution-of-the-identity (RI) and imaginary frequency integration techniques. We show that the RI approximation to four-index electron repulsion integrals leads to a variational upper bound to the exact RPA correlation energy if the Coulomb metric is used. Auxiliary basis sets optimized for second-order Möller-Plesset (MP2) calculations are well suitable for RPA, as demonstrated for the HEAT [1] and MOLEKEL [2] benchmark sets. Using imaginary frequency integration rather than diagonalization to compute the matrix square root necessary for RPA, evaluation of the RPA correlation energy requires \( O(N^4 \log N) \) operations and \( O(N^3) \) storage only; the price for this dramatic improvement over previous implementations is a numerical quadrature. We propose a numerical integration scheme that is exact in the two-orbital case and converges exponentially with the number of grid points. For most systems, 30-40 grid points yield \( \mu \text{H} \) accuracy in triple-zeta basis sets, but much larger grids are necessary for small-gap systems. The lowest-order approximation to the present method is a post-Kohn-Sham frequency domain version of opposite-spin Laplace-transform RI-MP2 [3]. Timings for polyacenes with up to 30 atoms show speed-ups of two orders of magnitude over previous implementations.
I. INTRODUCTION

The random phase approximation (RPA) to electron correlation energies is emerging\textsuperscript{4} as an important building block of accurate density functional treatments of for molecules and solids. In its simplest form, the RPA total energy

\[ E = E^{\text{HF}} + E^{\text{C RPA}}, \]

is a sum of the Hartree-Fock or exact exchange energy \( E^{\text{HF}} \) and the RPA correlation energy \( E^{\text{C RPA}} \). The RPA total energy is typically evaluated in a post-Kohn-Sham fashion, i.e. using Kohn-Sham orbitals from a preceding self-consistent generalized gradient approximation (GGA) or optimized effective potential (OEP) calculation. RPA combines a number of attractive features: (i) It includes long-range dispersion,\textsuperscript{5} as opposed to semi-local functionals, (ii) it is non-perturbative and can be applied to small or zero gap problems, such as metals\textsuperscript{6,7} or dissociating \( \text{H}_2 \),\textsuperscript{8} (iii) RPA is nearly exact in the high-density or low-coupling limit, and it is parameter-free, (iv) RPA is intimately related to Coupled Cluster doubles (CCD) theory.\textsuperscript{9,10} In applications, RPA is often combined with ”beyond-RPA corrections”, such as semi-local functionals with and without range separation,\textsuperscript{11–14} second order screened exchange,\textsuperscript{15} or local field corrections.\textsuperscript{16}

A central obstacle for the wide-spread use of RPA in electronic structure calculations is its relatively high computational cost. It became clear only recently that RPA may be implemented at a complexity similar to second-order Moller-Plesset (MP2) theory using sign function methods.\textsuperscript{17} Scuseria and co-workers proposed an algorithm based on Cholesky factorization of doubles amplitudes that should scale even more favorably than MP2;\textsuperscript{9} however, no general-purpose implementations of both methods appear to have been reported so far.

In the present work, we introduce the resolution-of-the-identity (RI) approximation to RPA correlation energies. If the Coulomb metric is used, RI-RPA has a variational upper bound property, making it stable and accurate in conjunction with basis sets optimized for RI-MP2. The RI approximation naturally leads to an imaginary frequency integration method to evaluate correlation energies. We present an implementation of the latter with \( O(N^4 \log N) \) operation count and \( O(N^3) \) storage requirements. The accuracy of our method is assessed using the HEAT\textsuperscript{1} and the larger MOLEKEL\textsuperscript{2} test sets which include most elements (H-Rn, except Lanthanides) in a variety of oxidation states. Performance benchmarks include polyacenes of increasing chain length.
II. THEORY

A. RPA correlation energy

The RPA correlation energy can be expressed in simple form using the plasmon equation:\textsuperscript{17}

\[ E^{C\text{RPA}} = \frac{1}{2} \text{tr}(\Omega - A), \]

(2)

where \( \Omega \) is a diagonal matrix containing the RPA excitation energies. The latter can be obtained from the symplectic eigenvalue problem\textsuperscript{18,19}

\[
\begin{pmatrix}
A & B \\
B & A
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
=
\begin{pmatrix}
\Omega & 0 \\
0 & -\Omega
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix},
\]

(3)

where the excitation vectors \( X \) and \( Y \) satisfy

\[ XX^T - YY^T = 1. \]

(4)

The so-called orbital rotation Hessian matrices \( A \) and \( B \) are given, within RPA,\textsuperscript{20} by

\[
(A - B)_{iajb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab},
\]

(5)

\[
(A + B)_{iajb} = (\epsilon_a - \epsilon_i)\delta_{ij}\delta_{ab} + 2\langle ia|jb\rangle.
\]

(6)

Here \( \epsilon \) is a Kohn-Sham orbital energy, \( \delta \) is the Kronecker delta, and \( \langle ia|jb\rangle \) is a two-electron integral in Mulliken notation. Indices, \( i, j, \ldots \) denote occupied and \( a, b, \ldots \) virtual molecular spin orbitals. We consider so-called direct RPA only, i.e. we do not include exchange integrals. All matrices have dimension \( N_{\text{occ}} \times N_{\text{virt}} \), where \( N_{\text{occ}} \) and \( N_{\text{virt}} \) are the number of occupied and virtual MOs and scale with the system size \( N \).

Within RPA, \( (A - B) \) is diagonal. It is well known from TDDFT\textsuperscript{18,21} that in this case Eq. 3 is easily transformed to a Hermitian eigenvalue problem

\[ MZ = \Omega^2Z, \quad ZZ^T = 1, \]

(7)

where

\[ M = (A - B)^{1/2}(A + B)(A - B)^{1/2}. \]

(8)

Thus, Eq. 2 may be rewritten in terms of the square root of \( M \),

\[ E^{C\text{RPA}} = \frac{1}{2} \text{tr}(M^{1/2} - A). \]

(9)
While $M$ has only half the dimension of the superoperators in Eq. 3, computation of $M^{1/2}$ by complete diagonalization scales as $O(N^6)$; this may be improved to $O(N^5)$ using iterative sign function methods.\textsuperscript{17}

Scuseria, Henderson and Sorenson recently pointed out\textsuperscript{9} that Eqs. 2, 3 and 7 are equivalent to

$$E^{\text{C RPA}} = \frac{1}{2} \text{tr}(BT),$$

(10)

where the matrix of doubles amplitudes $T$ satisfies a truncated Coupled Cluster Doubles (CCD) equation,

$$B + AT + TA + TBT = 0.$$  \hfill (11)

Without further approximations, the operation count for an iterative solution of Eq. 11 scales as $O(N^5)$ if integral-direct methods are used. Both the matrix square root and the CCD approach require handling and repeated storage of $O(N^4)$ arrays, which hampered applications to systems with more than approximately 30 atoms in the past.

**B. Resolution-of-the-Identity approximation**

The Resolution-of-the-Identity (RI) approximation\textsuperscript{22} based on the Coulomb metric\textsuperscript{23} has been very successful in reducing the cost of non-hybrid ground-state DFT\textsuperscript{24} and TDDFT excitation energy\textsuperscript{25–27} calculations by 1-2 orders of magnitude without significant loss of accuracy. The central idea of RI-methods is to approximately factorize the four-center integrals $(ia|jb)$ according to

$$(ia|jb)_{RI} = \sum_{PQ} (ia|P)(P|Q)^{-1}(Q|jb),$$

(12)

where $P, Q$ denote atom-centered Gaussian auxiliary basis functions. For fixed ground-state orbitals and excitation vectors, the RI error in any RPA excitation energy is quadratic in the auxiliary basis set error\textsuperscript{27}.

This variational stability implies that high accuracy in excitation energies can be achieved with moderately sized auxiliary basis sets, and it permits systematic optimization of such basis sets. As shown in Appendix A the variational stability carries over to the RI-RPA correlation energy $E^{\text{C RIRPA}}$

$$E^{\text{C RIRPA}} = E^{\text{C RPA}} + \sum_n ||\rho_n - \rho_n^{RI}||_C^2,$$

(13)
where the densities $\rho_n$ are defined in Appendix A, and $\| \cdot \|_C$ denotes the Coulomb metric. In other words, the RI-RPA correlation energy is a variational upper bound of the exact RPA correlation energy, as long as the orbitals and excitation vectors are kept fixed. This may be compared to RI-MP2 theory, where such a bound does not exist due to exchange terms not present in RPA. In practice, orbitals and excitation vectors will be computed using RI as well, leading to additional errors linear and quadratic in the auxiliary basis. The magnitude of these errors will be addressed in Sec. IV A.

The RI approximation exploits the rank deficiency of the two-electron integrals $(ia|jb)$. This is obvious from the factorization

$$(ia|jb)_{RI} = \sum_P S_{iaP} S_{jbQ},$$

where $S_{iaP} = \sum_Q (ia|Q)L_{QP}$ and $L_{QP}$ is determined by the Cholesky decomposition of the two-electron integrals $(P|Q)$. Since the number of auxiliary basis functions $N_{aux}$ increases only linearly with $N$, it is much more efficient to work with matrix $S$ instead of the full two-electron matrix $(ia|jb)$. A straightforward way of using the RI-approximation for RPA correlation energy calculations is to replace the two-electron matrix in Eq. 8 by $SS^T$, which defines the RI-RPA correlation energy, $E^{CRI RPA}$. While this simple strategy drastically reduces integral evaluation costs, it does not improve scaling, because the two-electron matrix $(ia|jb)_{RI}$ still is explicitly constructed. To bypass the $O(N^5)$ CPU and $O(N^4)$ I/O bottlenecks of conventional RPA, an algorithm which entirely avoids four-index quantities is necessary.

C. Efficient evaluation of $E^{CRI RPA}$ using quadrature

We aim to evaluate the RI-RPA correlation energy by making explicit use of the rank deficiency of $(ia|jb)_{RI}$. Inspired by Casimir and Polders early work on $C_6$ coefficients,\textsuperscript{5,28} we express $M^{1/2}$ by an integral following Higham and Trefethen$^{29}$

$$\text{tr } (M^{1/2}) = \int_{-\infty}^\infty \frac{d\omega}{2\pi} \text{tr } \left( 1 - \omega^2 (M + \omega^2 1)^{-1} \right) = \int_{-\infty}^\infty \frac{d\omega}{2\pi} f(\omega).$$

(15)

Since $M = D^2 + 2D^{1/2}SS^T D^{1/2}$, where $D_{iajb} = D_{ia}\delta_{ij}\delta_{ab}$, $D_{ia} = (\epsilon_a - \epsilon_i)$, is the diagonal matrix of bare orbital energy differences, the inverse of $M + \omega^2 1$ may be rewritten as

$$(M + \omega^2 1)^{-1} = D^{-2}G(\omega) - 2D^{-1/2}G(\omega)S [(I_{aux} + 2Q(\omega))^{-1}] S^T G(\omega) D^{-1/2},$$

(16)
where

$$G(\omega) = D(D^2 + \omega^2 \mathbf{1})^{-1} \quad (17)$$

is diagonal in the canonical Kohn-Sham orbital basis, and

$$Q(\omega) = 2S^T G(\omega) S \quad (18)$$
is an $N_{aux} \times N_{aux}$ matrix. Straightforward computation of $Q(\omega)$ from Eq. 14 scales as $O(N^4)$. The key observation is that, within the RI approximation, the trace of $(M + \omega^2 \mathbf{1})^{-1}$ and thus the integrand $f(\omega)$ may be evaluated with $O(N^4)$ operations using at most three-index quantities. If the integral in Eq. 15 can be approximated by quadrature with a small number of grid points $N_g$, this method requires $O(N^4 N_g)$ operations and $O(N^3)$ storage only to compute RI-RPA correlation energies.

Instead of evaluating $\text{tr} (M^{1/2})$ and subtracting $\text{tr} (A)$ afterwards, it is much more efficient and numerically stable to express $\text{tr} (A)$ as an integral similar to Eq. 15 and to subtract the integrands. Thus,

$$\text{tr} (A) = \text{tr} \left( [D^2]^{1/2} \right) + \text{tr} (SS^T), \quad (19)$$

where we use Eq. 15 to write

$$\text{tr} \left( [D^2]^{1/2} \right) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \left( 1 - \omega^2 D^{-2} G(\omega) \right) \quad (20)$$

Using the residue theorem, it is straightforward that

$$\text{tr} (SS^T) = 2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \left( D^{-1/2} G(\omega) SS^T G(\omega) D^{-1/2} \right) \quad (21)$$

The RI-RPA correlation energy can thus be obtained from

$$E^{\text{C RIRPA}} = \frac{1}{2} \left( \text{tr} (M^{1/2}) - \text{tr} (A) \right) \quad (22)$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f^c(\omega), \quad (23)$$

where the RI-RPA correlation energy integrand

$$f^c(\omega) = -2\omega^2 \text{tr} \left( D^{-1/2} G(\omega) S \left[ 1 - (1_{aux} + Q(\omega))^{-1} \right] S^T G(\omega) D^{-1/2} \right) \quad (24)$$

$$= 2\omega \text{tr} \left( Q'(\omega) \left[ 1 - (1_{aux} + Q(\omega))^{-1} \right] \right)$$
is much smaller in magnitude and shorter ranged than $f(\omega)$. Since

$$Q'(\omega) = 2S^T G'(\omega) S = -4\omega S^T D(D^2 + \omega^2 \mathbf{1})^{-2} S \quad (25)$$
is the derivative of $Q(\omega)$, and $Q(\omega)$ vanishes as $\omega^{-2}$ for large $\omega$, it is possible to perform a partial integration on $f^c(\omega)$, leading to a central result of the present work:

$$
E^{\text{C RIRPA}} = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \text{tr} \left( \ln (1_{\text{aux}} + Q(\omega)) - Q(\omega) \right) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} F^C(\omega). \quad (26)
$$

At first sight, it appears that this result could have been obtained more directly from Langreth's and Perdew's original expression

$$
E^{\text{C RPA}} = \Im \int_{-\infty}^{\infty} \frac{d(i\omega)}{2\pi} \text{tr} \left( \ln (1 + \chi(i\omega)W) - \chi(i\omega)W \right), \quad (27)
$$

where $\chi$ is the Kohn-Sham density-density response function and $W$ is the bare Coulomb interaction. In fact, Eq. 27 has been used for years to evaluate RPA correlation energies in plane-wave implementations,\cite{6, 31, 32} where auxiliary basis expansions are straightforward, and in numerical calculations for atoms.\cite{11, 33} However, the present treatment reveals two important new results: First, it establishes the strict equivalence of Eq. 26 and the plasmon formula, Eq. 2, in finite (auxiliary) basis sets. Thus, the variational upper bound property of RI-RPA holds for Eq. 26 too. Second, the present analysis shows the analytical structure of the integrand in $F^C(\omega)$: Using the spectral representation of $M$, Eq. 26 becomes

$$
E^{\text{C RIRPA}} = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \sum_{ia} \left( \ln \left( 1 + \frac{\Omega^2_{ia} - D^2_{ia}}{\omega^2 + D^2_{ia}} \right) - \frac{\Omega^2_{ia} - D^2_{ia}}{\omega^2 + D^2_{ia}} \right). \quad (28)
$$

Knowledge of the analytical structure of the integrand will turn out to be crucial for constructing efficient quadratures for $E^{\text{C RIRPA}}$.

### D. Numerical Integration Scheme

We use Clenshaw-Curtis quadrature\cite{34} to evaluate the frequency integral in Eq. 26. This quadrature consists of a mapping

$$
\omega = a \cot t; \quad 0 \leq t \leq \pi \quad (29)
$$

to the interval $[0, \pi]$ where $a$ is a scaling parameter. The integrand $F^C(\omega)$ decays as $1/\omega^4$ for large $\omega$ and thus $F^C(a \cot t)$ vanishes at the end points $t = 0, \pi$. Since $F^C(a \cot t)$ is periodic, the trapezoid rule converges exponentially,\cite{34} leading to the RI-RPA correlation energy approximated by numerical integration (NI)

7
\[
E_{\text{NI}}^{\text{RIRPA}} = \sum_{j=1}^{N_g} \frac{w_j}{2\pi} F^C(a \cot t_j),
\]
(30)
\[
t_j = \frac{j \pi}{N_g}, \quad j = 1, \ldots, N_g,
\]
(31)
\[
w_j = \begin{cases} 
\frac{a\pi}{N_g\sin^2 t_j}; & j = 1, \ldots, N_g - 1 \\
\frac{a\pi}{2N_g\sin^2 t_j}; & j = N_g 
\end{cases}
\]
(32)

Here the integration was restricted to the interval \([0, \frac{\pi}{2}]\) using that \(F^C(\omega)\) is even.

As opposed to e.g., Laplace-transform MP2-theory,\(^{35}\) the RPA integrand \(F^C(\omega)\) depends on both, the bare orbital energy differences \(D_{ia}\) and the full RPA excitation energies \(\Omega_{ia}\). Since the latter are not known \textit{a priori}, it is difficult to compute optimal integration grids in the spirit of Almlöf’s and Häser’s least squares method.\(^{35}\) However, we can construct an approximation to \(F^C(\omega)\) by replacing \(M\) by its diagonal. Using the spectral methods introduced in section II C, we obtain the diagonal approximation to \(F^C(\omega)\),
\[
F^D(\omega) = \sum_{ia} \ln \left( 1 + \frac{M_{iaia} - D_{ia}^2}{\omega^2 + D_{ia}^2} \right) - \frac{M_{iaia} + D_{ia}^2}{\omega^2 + D_{ia}^2},
\]
(33)

where \(M_{iaia} = D_{ia}^2 + 2D_{ia}(ia|ia)\) is the diagonal of \(M\). We determine the free parameter \(a\) by the constraint that \(F^D(\omega)\) is integrated exactly,
\[
\sum_{j=1}^{N_g} \frac{w_j}{2\pi} F^D(a \cot t_j) = \frac{1}{2} \sum_{ia} \left[ \sqrt{M_{iaia}} - (D_{ia} + (ia|ia)) \right].
\]
(34)

This non-linear equation for \(a\) has at least one solution, which can be determined at \(O(N^2)\) cost using the Newton-Raphson method. Our approach ensures that the overall distribution of the grid points is adapted to the eigenvalue spectrum of \(M\) and \(D\). However, if the condition number of \(M^{1/2}\),
\[
\kappa = \frac{\Omega_{\text{max}}}{\Omega_{\text{min}}},
\]
(35)
becomes large, the scales of the contributions to \(F^C\) from different eigenvalues become very different, and a large number of points is required for high accuracy.
E. Relation to Laplace-transform MP2

Taylor expansion of the logarithm in Eq. 26 around $Q(\omega) = 0$ yields the perturbation expansion of $E^{C_{\text{RIRPA}}}$ in powers of the electron interaction. The first non-vanishing terms,

$$E^{C(2)} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} Q^2(\omega) = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \sum_{iajb} G_{ia}(\omega)(ia|jb)^2_{\text{RI}} G_{jb}(\omega)$$

$$= - \frac{1}{2} \sum_{iajb} (ia|jb)^2_{\text{RI}} \frac{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}{RI},$$

(36)

is identical to the direct (Hartree) doubles part of Second-order Görling-Levy (GL2) perturbation theory within the RI approximation.

The Fourier transform of $G(\omega)$ is

$$\hat{G}(t) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} G(\omega) = \frac{1}{2} e^{-D'|t|},$$

(37)

where the caret symbol denotes Fourier-transformed quantities.

Since both $G(\omega)$ and $\hat{G}(t)$ are real, $E^{C(2)}$ may be expressed in terms of $\hat{G}(t)$ using Parseval’s theorem,

$$E^{C(2)} = - \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} |Q(\omega)|^2 = - \int_{-\infty}^{\infty} dt |\hat{Q}(t)|^2$$

$$= - \frac{1}{4} \int_{-\infty}^{\infty} dt \sum_{iajb} e^{-D_a|t|}(ia|jb)^2_{\text{RI}} e^{-D_b|t|}$$

$$= - \frac{1}{2} \int_{0}^{\infty} dt \sum_{iajb} e^{-(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)t}(ia|jb)^2_{\text{RI}}.$$

(38)

This is the Laplace-transform version of $E^{C(2)}$. Laplace-transform methods were first used by Almlöf and Häser to evaluate MP2 correlation energies in an $O(N^4)$ algorithm, and are now fairly common in MP2 implementations for molecules and solids aiming at large systems. The scaled opposite-spin (SOS) MP2 method by Jung, Lochan, Dutoi and Head-Gordon combines Laplace-transform with RI methods and is identical to Eq. 36 up to a scaling factor if HF instead of KS orbitals are used. Thus, Eq. 36 may be considered as a frequency-domain version of opposite-spin Laplace-transform RI-MP2. Beyond second order, the use of the Fourier transform $\hat{Q}(t)$ instead of $Q(\omega)$ in Eq. 26 requires multiple integrations over $t$ and thus becomes inefficient.
F. Relation to Coupled-Cluster theory

By comparison of Eqs. 2 and 26, the RI approximation to the cluster amplitudes $T$ may be identified,

$$ T^{\text{RI}} = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} G(\omega) S R(\omega) S^T G(\omega), $$

where

$$ R(\omega) = 4 Q^{-2}(\omega) \left( \ln(1 + Q(\omega)) - Q(\omega) \right) $$

is $N_{\text{aux}} \times N_{\text{aux}}$ only. Thus, the low rank of $(ia|jb)_{\text{RI}}$ carries over to $T^{\text{RI}}$ if the integral in Eq. 39 may be efficiently approximated by quadrature. Eq. 39 could be used to evaluate second-order screened exchange (SOSEX) corrections to RPA; if exchange-type contractions are computed in an integral direct fashion, this method scales as $O(N^4 \log N)$.

III. COMPUTATIONAL DETAILS

Eq. 30 was implemented in the rimp2 module of TURBOMOLE. RI-MP2 energies were obtained using the same module, whereas the module mpgrad was used to calculate MP2 and RPA correlation energies without the RI approximation. All RPA calculations used Kohn-Sham PBE orbitals as input; they were performed in C1 symmetry. The density matrix convergence criterion was set to $10^{-8}$ a.u. Tight grids (m5) were used throughout. Core electrons were kept frozen, unless otherwise stated.

We used Dunning’s (augmented) correlation consistent basis sets along with Karlsruhe basis sets of split valence and triple zeta quality with extra polarization functions (def2-TZVPP). RI-MP2 auxiliary basis sets optimized for the corresponding MO-basis sets were used, except otherwise stated.

The HEAT and MOLEKEL test sets were chosen to assess the accuracy of the RI approximation and the performance of the numerical integration. HEAT consists of atoms H, C, N, O, F and small molecules and is constructed for thermochemistry. The MOLEKEL test set contains nearly all elements (H-Rn, except Lanthanides) in nearly all common oxidation states. CH$_2$ was excluded from HEAT and NbF3 from MOLEKEL due to negative orbital energy differences.
IV. RESULTS

A. Accuracy the RI approximation

Fig. 1 shows the absolute error in the RI-RPA correlation energy of \( \text{N}_2 \) (no frozen core) as a function of the auxiliary basis set size. The orbital basis (aug-cc-pVTZ) is kept constant here. The RI error decreases rapidly with auxiliary basis set size, as expected from the quadratic dependence of the RI-RPA correlation energies on the auxiliary expansion error, Eq. 13. The MP2 errors are generally smaller, but of the same order of magnitude as the errors in RPA.

Figs. 2 and 3 show errors in RI-RPA correlation energy for the HEAT test set including all electrons. The error decreases quickly with increasing auxiliary basis set size. Here orbital basis sets consistent with the auxiliary basis sets were used. Fig. 3 compares RI errors of RPA and MP2 using the aug-cc-pVTZ and aug-cc-pVQZ basis sets. The errors due to RI are larger for RPA energies, but again of the same order of magnitude as the errors in MP2 energies. The mean correlation energies for aug-cc-pVTZ for HEAT are \( E_{\text{mean}}^{\text{MP2}} = -0.310 \) hartree and \( E_{\text{mean}}^{\text{RPA}} = -0.507 \) hartree. The smaller RI error for MP2 reflect that the auxiliary basis sets were optimized for MP2, not RPA, and the considerably larger absolute value of RPA compared to MP2 correlation energies. Due to the variational upper bound, Eq. 13, the RI errors are always positive in RPA, but not in MP2. Even in the triple zeta case the errors are in the micro-hartree range for all systems.

Errors in HEAT atomization energies are shown in Fig. 4. The absolute error in these energy differences is slightly smaller due to cancellation. HEAT reaction energies for the reactions in Table V of Ref [1] using cc-pVTZ were computed and are all less than 100 \( \mu \)H. We conclude that the errors due to RI are approximately 2 orders of magnitude smaller then orbital basis set errors and intrinsic errors of RPA. Auxiliary basis sets optimized for MP2 are safe to use for RPA, although somewhat larger errors must be expected.

B. Accuracy of the quadrature

Fig. 5 shows the absolute error in RI-RPA atomization energies due to numerical integration on the HEAT set using cc-pVTZ basis sets. The accuracy increases exponentially with the number of grid points, as expected. However, the magnitude of the error varies
considerably depending on the system. In many cases 20 or less points are sufficient for sub-millihartree accuracy, whereas in others, such as CF, F$_2$, NO and OF 40 grid points are required. The latter systems have a relatively small gap, leading to a large condition number $\kappa$. As a consequence, the convergence with the number of grid points is slow in these cases. This is illustrated in Fig. 6 HEAT RI-RPA correlation energies using cc-pVTZ and 20 grid points. The condition number correlates well with the RI error.

Table I compares the mean error (ME), mean absolute error (MAE) and the maximum error (Max) for HEAT RI-RPA atomization energies with increasing grid size for different basis sets. For comparison results for the error due to introducing RI are presented as well. Obviously, larger basis sets require larger grids, because higher excitations increase the condition number $\kappa$. The error due to RI (final column) is consistently low (sub millihartree) for all basis sets. To reach errors of the same order of magnitude 30 grid points are needed for cc-pVDZ, approximately 35 for cc-pVTZ and more than 40 for cc-pVQZ and cc-pV5Z. The quadrature error is much less uniform then RI error. For consistent accuracy on the order of magnitude of the RI error, we recommend using at least 35 grid points for triple zeta basis sets.

Larger grids are necessary for all-electron calculations, because $x$ increases as core excitations are included. As summarized in Table II, the maximum error for HEAT using cc-pVTZ basis sets is still in the millihartree range for $N_g = 40$.

Finally, results on the accuracy of the numerical integration for the MOLEKEL test set are presented in Table III for the def2-TZVPP basis with increasing grid size. The MAE is below 1 mH for a 35 point grid. However, there are cases with small gaps that require much larger grids. We conclude that the numerical integration method is efficient for condition numbers $\kappa$ below approximately 500, but fails for small gap systems.

C. Performance

To assess the performance of our method timings and memory requirements for the computation of the RPA correlation energy for a series of linear polyacenes are shown in Table IV. Def2-TZVPP basis sets and $N_g = 40$ were used. Table V displays the quadrature errors in RI-RPA correlation energies as a function of grid size. For all systems sub-millihartree accuracy is reached with 20 grid points. The quadrature error increases approximately linearly
with the system size, but decreases exponentially with the number of grid points. This is consistent with an $O(\log N)$ increase in quadrature points for constant absolute and an $O(1)$ increase for constant relative accuracy. The timings clearly demonstrate the potential of evaluating the RPA correlation energy using RI and numerical integration. For tetracene full diagonalization takes approximately 10 hours on a single CPU of a Xeon X5560 2.80MHz workstation, whereas the frequency integration takes just about 17 minutes, which amounts to a 35-fold speed-up. The memory and storage requirements are also reduced by an order of magnitude.

V. CONCLUSIONS

In direct RPA, the RI approximation leads to a variational upper bound for the correlation energy if the Coulomb metric is used. The main differences between MP2 and RPA are the gap size, which is typically larger in MP2, and the presence of self-interaction in RPA. Both lead to RPA correlation energies (and thus RI errors) significantly larger than MP2 correlation energies. Nevertheless, due to the variational stability of RI-RPA, auxiliary basis sets optimized for RI-MP2 calculations yield RI errors comparable to those of RI-MP2 when used for RI-RPA calculations.

RI-RPA correlation energies may be evaluated in an $O(N^4 \log N)$ algorithm based on imaginary frequency integration. While this technique has been used for RPA before, a key result of the present paper is that at most three-index quantities are required if the RI approximation is used. This is remarkable since there are $O(N^2)$ RPA excitation energies, yet the rank of all occurring matrices is at most $O(N)$. The approach is viable because, even though there are $O(N^2)$ excitation energies, they are spread over a finite interval that scales approximately as $O(1)$, and thus the sum in Eq. 2 may be approximated by quadrature using a constant number of grid points. While most systems require 20-30 grid points only for sum-mH accuracy, the quadrature becomes inefficient if the condition number $\kappa$ is large. For such cases a hybrid approach appears promising, where a few of the extreme eigenvalues of $M$ are determined explicitly, and the quadrature is applied to the remainder of $M$, which has a much smaller condition number.

The lowest order approximation to the present method is a KS-based frequency-domain version of the opposite-spin Laplace-transform RI-MP2 method by Jung, Lochan, Dutoi
and Head-Gordon. The close connection of RPA to Coupled Cluster theory suggests that imaginary frequency integration techniques might be useful for other non-perturbative correlated wavefunction treatments beyond RPA.

Acknowledgments

We thank Florian Weigend and Dmitrij Rappoport for providing input files for the MOLEKEL test set. This work was supported by the National Science Foundation, grant No. CHE-0911266.

APPENDIX A: VARIATIONAL UPPER BOUND PROPERTY OF THE RI-RPA CORRELATION ENERGY

We start from the RI version of Eq. 10,

\[ E^{CRI RPA} = \frac{1}{2} \sum_{iajb} (ia|jb)^{RI} T_{iajb}. \]  

(A1)

The \( T \) amplitudes are determined by the excitation vectors according to \( T = XY^{-1} \) [9] and thus kept fixed for the moment. Thus,

\[
E^C_{RPA} - E^{CRI RPA} = \frac{1}{2} \left[ (ia|jb) - (ia|jb)^{RI} \right] T_{iajb} \\
= \frac{1}{2} \sum_{iajb} \left[ (ia|jb) - 2 \sum_{PQ} (ia|P)(P|Q)^{-1}(Q|jb) \right. \\
+ \left. \sum_{PQRS} (ia|P)(P|Q)^{-1}(Q|R)(R|S)^{-1}(S|jb) \right] T_{iajb}.
\]

(A2)

Since, within RPA, \(-T\) is symmetric and positive definite, a Cholesky factorization

\[ T_{iajb} = - \sum_n V_{ian} V_{ian} \]  

(A3)

exists, and Eq. A2 may be rewritten as

\[
E^C_{RPA} - E^{CRI RPA} = - \sum_n \frac{1}{2} \int d^3r d^3r' \left[ \rho_n(r) - \rho_n^{RI}(r) \right] \left[ \rho_n(r') - \rho_n^{RI}(r') \right] \\
\|r - r'\| C, 
\]

(A4)
where
\[ \rho_n(r) = \sum_{i\alpha\sigma} V_{i\alpha n}(r, \sigma) \phi_i(r, \sigma), \] (A5)
is the density of the Cholesky vector \( V_{i\alpha n} \) expanded in a spin orbital basis \( \{\phi_i\} \), and
\[ \rho_{n}^{RI}(r) = \sum_{i\alpha\sigma} V_{i\alpha nPQ}(i\alpha|P)(P|Q)^{-1}\chi(r), \] (A6)
is its expansion in an auxiliary basis \( \{\chi_Q\} \). \( || \cdot ||_C \) is the Coulomb norm whose square is the Hartree energy. Thus
\[ E^{CRI\text{ RPA}} = E^{C\text{ RPA}} + \sum_n ||\rho_n - \rho_{n}^{RI}||_C^2, \] (A7)
i.e. \( E^{CRI\text{ RPA}} \) is a variational upper bound for \( E^{C\text{ RPA}} \) for fixed excitation vectors and ground-state orbitals.

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Fig. 1: Absolute RI errors for RPA and RI-RPA ($|E^C_{RI-RPA} - E^C_{RPA}|$), and for MP2 ($|E^C_{RI-MP2} - E^C_{MP2}|$), for $\text{N}_2$ with varying auxiliary basis set. No electrons were frozen. Kohn-Sham orbitals using PBE have been used for RPA, and HF orbitals for MP2, all using the aug-cc-pVTZ basis.
FIG. 2: RI errors ($\Delta E = E_{RI-RPA} - E_{RPA}$) for the HEAT test set for three of Dunning’s correlation consistent basis sets (AVTZ = aug-cc-pVTZ, etc.). No electrons were frozen. Kohn-Sham/PBE orbitals have been used as input.
FIG. 3: RI errors for RPA and MP2 for the HEAT test set for two of Dunning’s correlation consistent basis sets (AVTZ = aug-cc-pVTZ, etc.). No electrons were frozen. Kohn-Sham/PBE orbitals have been used as input for RPA, HF orbitals for MP2.

FIG. 4: RI errors for HEAT atomization energies for RPA and MP2 using the aug-cc-pVTZ basis set. Kohn-Sham/PBE orbitals have been used as input for RPA, HF orbitals for MP2.
FIG. 5: Absolute errors in atomization energies due to numerical integration for the HEAT test set (cc-p-VTZ) as a function of the number of grid points $N_g$. 
FIG. 6: Error in $E^{CRIRPA}$ energies due to numerical integration ($N_g = 20$) for the HEAT test set (cc-pVTZ) compared to the condition number $\kappa = \Omega_{\text{max}}/\Omega_{\text{min}}$.

TABLES

TABLE I: Mean errors (ME), mean absolute errors (MAE), and maximum errors (Max) for the HEAT test set with varying number of grid points $N_g$ and increasing basis set size ($VXZ = \text{cc-pVXZ}$). The last column contains the RI error.

<table>
<thead>
<tr>
<th>$N_g$</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>-3.637E-04</td>
<td>2.112E-04</td>
<td>3.738E-05</td>
<td>5.618E-06</td>
<td>1.218E-04</td>
</tr>
<tr>
<td>VDZ</td>
<td>3.811E-03</td>
<td>3.280E-04</td>
<td>4.082E-05</td>
<td>5.725E-06</td>
<td>1.226E-04</td>
</tr>
<tr>
<td>Max</td>
<td>2.618E-02</td>
<td>3.922E-03</td>
<td>6.301E-04</td>
<td>1.032E-04</td>
<td>2.400E-04</td>
</tr>
<tr>
<td>ME</td>
<td>-3.763E-03</td>
<td>1.415E-04</td>
<td>1.060E-04</td>
<td>2.892E-05</td>
<td>7.398E-05</td>
</tr>
<tr>
<td>VTZ</td>
<td>8.208E-03</td>
<td>1.008E-03</td>
<td>1.675E-04</td>
<td>3.336E-05</td>
<td>7.404E-05</td>
</tr>
<tr>
<td>Max</td>
<td>3.569E-02</td>
<td>7.880E-03</td>
<td>1.867E-03</td>
<td>4.544E-04</td>
<td>1.540E-04</td>
</tr>
<tr>
<td>ME</td>
<td>-5.824E-03</td>
<td>-2.867E-04</td>
<td>1.011E-04</td>
<td>5.315E-05</td>
<td>2.551E-05</td>
</tr>
<tr>
<td>VQZ</td>
<td>1.160E-02</td>
<td>1.995E-03</td>
<td>4.606E-04</td>
<td>1.314E-04</td>
<td>2.552E-05</td>
</tr>
<tr>
<td>Max</td>
<td>4.533E-02</td>
<td>1.212E-02</td>
<td>3.859E-03</td>
<td>1.230E-03</td>
<td>6.546E-05</td>
</tr>
<tr>
<td>ME</td>
<td>-7.357E-03</td>
<td>-7.416E-04</td>
<td>5.053E-05</td>
<td>8.682E-05</td>
<td>1.722E-05</td>
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<tr>
<td>V5Z</td>
<td>1.440E-02</td>
<td>2.976E-03</td>
<td>7.945E-04</td>
<td>2.470E-04</td>
<td>1.753E-05</td>
</tr>
<tr>
<td>Max</td>
<td>5.247E-02</td>
<td>1.567E-02</td>
<td>5.737E-03</td>
<td>2.259E-03</td>
<td>3.688E-05</td>
</tr>
</tbody>
</table>

TABLE II: Mean errors (ME), mean absolute errors (MAE), and maximum errors (Max) for the HEAT test set with varying number of grid points $N_g$ using cc-pVTZ, either freezing core electrons (fr. core) or including core electrons (all e). The last column contains the RI error.

<table>
<thead>
<tr>
<th>$N_g$</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>RI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>-3.763E-03</td>
<td>1.415E-04</td>
<td>1.060E-04</td>
<td>2.892E-05</td>
<td>7.398E-05</td>
</tr>
<tr>
<td>fr. core</td>
<td>8.208E-03</td>
<td>1.008E-03</td>
<td>1.675E-04</td>
<td>3.336E-05</td>
<td>7.404E-05</td>
</tr>
<tr>
<td>Error</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>R</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>MAE</td>
<td>2.368E-03</td>
<td>9.667E-04</td>
<td>4.817E-04</td>
<td>2.551E-04</td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>3.967E-01</td>
<td>2.172E-01</td>
<td>1.246E-01</td>
<td>8.855E-04</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE III:** Mean absolute errors (MAE), and maximum errors (Max) for the MOLEKEL test set with varying number of grid points \( N_g \) for the def2-TZVPP basis set. The mean error is equal to then MAE. The last column (RI) contains the RI error.

**TABLE IV:** Timings (hours, minutes, seconds) and memory requirements (megabytes) for the calculation of \( E^{\text{CRIRPA}} \) either by full diagonalization (diag) or by numerical integration (NI) for a set of polyacenes of increasing size. Def2-TZVPP and \( N_g = 40 \) were used, and the calculations were performed on a single CPU of a Xeon X5560 2.80Mhz workstation. The memory listed is the memory needed for storage of the four-index object in case of diagonalization or the three-index object in case of numerical integration.

<table>
<thead>
<tr>
<th>system</th>
<th>( N_{\text{occ}} \times N_{\text{virt}} )</th>
<th>( t^{\text{diag}} )</th>
<th>( t^{\text{NI}} )</th>
<th>( \text{mem}^{\text{diag}} )</th>
<th>( \text{mem}^{\text{NI}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene (C(_6)H(_6))</td>
<td>3735</td>
<td>1’ 24”</td>
<td>30”</td>
<td>100</td>
<td>44</td>
</tr>
<tr>
<td>naphthalene (C(_{10})H(_8))</td>
<td>9312</td>
<td>24’ 3”</td>
<td>2’ 17”</td>
<td>630</td>
<td>167</td>
</tr>
<tr>
<td>anthracene (C(<em>{14})H(</em>{10}))</td>
<td>17391</td>
<td>2 33’ 6”</td>
<td>6’ 48”</td>
<td>2250</td>
<td>420</td>
</tr>
<tr>
<td>tetracene (C(<em>{18})H(</em>{12}))</td>
<td>27972</td>
<td>10 0’ 59”</td>
<td>16’ 31”</td>
<td>6500</td>
<td>851</td>
</tr>
</tbody>
</table>

**TABLE V:** Errors in \( E^{\text{CRIRPA}} \) due to numerical integration for the polyacene series with increasing gridsize \( N_g \). The def2-TZVPP and corresponding auxiliary basis sets were used.

<table>
<thead>
<tr>
<th>( N_g )</th>
<th>benzene</th>
<th>naphthalene</th>
<th>anthracene</th>
<th>tetracene</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-6.435E-04</td>
<td>-2.382E-03</td>
<td>-7.958E-03</td>
<td>-2.253E-02</td>
</tr>
<tr>
<td>30</td>
<td>-1.291E-06</td>
<td>-7.662E-06</td>
<td>-4.132E-05</td>
<td>-1.331E-04</td>
</tr>
<tr>
<td>40</td>
<td>-5.065E-08</td>
<td>-6.225E-07</td>
<td>-5.349E-06</td>
<td>-2.695E-05</td>
</tr>
</tbody>
</table>