Correlation Energies from the Two-Component Random Phase Approximation

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ⓈSupporting Information

ABSTRACT: The correlation energy within the two-component random phase approximation accounting for spin−orbit effects is derived. The resulting plasmon equation is rewritten—analogously to the scalar relativistic case—in terms of the trace of two Hermitian matrices for (Kramers-restricted) closed-shell systems and then represented as an integral over imaginary frequency using the resolution of the identity approximation. The final expression is implemented in the TURBO-MOLE program suite. The code is applied to the computation of equilibrium distances and vibrational frequencies of heavy diatomic molecules. The efficiency is demonstrated by calculation of the relative energies of the O_h-, D_{4h}-, and C_{5v}-symmetric isomers of Pb_6. Results

Two-component (2c) RPA correlation energy

$$E_C^{2c\ RPA} = \frac{1}{2} \sum_n \left(\omega_n^{2c\ RPA} - \omega_n^{2c\ TDA\ RPA} \right)$$

within the random phase approximation are obtained based on two-component Kohn−Sham reference-state calculations, using effective-core potentials. These values are finally compared to other two-component and scalar relativistic methods, as well as experimental data.

1. INTRODUCTION

The random phase approximation (RPA) is an increasingly popular post−Kohn−Sham method that is used to accurately calculate the correlation energy; thus, it has become a major field of research in quantum chemistry in the past few years.[1−6] RPA has many attractive features: (i) it includes long-range dispersion;[7] (ii) it can be applied to small- or zero-gap systems, such as metals[8,9] or dissociating H_2,[10] as opposed to perturbative methods; and (iii) it is parameter-free. Since the first application of RPA to molecules using a Kohn−Sham reference by Furche,[11] computationally appealing formulations of the RPA correlation energy, both in context of density functional theory (DFT)[12] and the ring-coupled-cluster-doubles (rCCD)[13] (without exchange), have been developed. Finally, RPA was made applicable to large systems by an efficient implementation[1,14] in the TURBOMOLE program package,[15] using the representation of the RPA correlation energy as an integral over imaginary frequency,[16] in combination with the resolution of the identity (RI) approximation[14] and an exponentially converging Clenshaw−Curtis quadrature.[17]

Relativistic methods have also been an important field of research in the past years. Mostly, the incorporation of relativistic effects is limited to scalar relativistic effects since it does not change the structure of existing quantum-chemical programs. As in non-relativistic theories, one-component scalar relativistic (1c) real molecular orbitals (MOs) can be used. However, in 1c methods, the effect of spin−orbit coupling (SOC), which leads to a splitting of the 1c energy levels, is neglected.

The most fundamental way to include SOC is by utilizing a fully relativistic theory (e.g., that based on the Dirac−Coulomb

Hamiltonian), using four-component (4c) complex spinors. A more economic alternative, with a very similar accuracy, for chemical applications are quasi-relativistic theories using two-component (2c) complex spinors. Within a 2c theory SOC (as well as 1c) contributions have mainly been incorporated by the all-electron zeroth-order regular approximation (ZORA),[18−21] the all-electron exact 2c (X2C) approach,[22−29] or, most efficiently, 2c Dirac−Fock effective core potentials (dhf-ECPs). 2c dhf-ECPs are fitted to 4c multiconfiguration Dirac−Hartree−Fock calculations on atoms and are available for elements beyond Kr.[30−36] In contrast to all-electron methods, only valence electrons have to be treated explicitly within the calculations, which leads to significant savings in computation time.

Recently, several 2c methods based on ECPs and/or X2C[37] have been implemented in the TURBOMOLE program package, taking into account SOC in a highly efficient manner: DFT and Hartree−Fock (HF) ground-state methods,[38] (explicitly correlated) second-order Møller−Plesset perturbation theory (MP2),[39] and time-dependent density functional theory (TDDFT).[40]

Therefore, the goal of this work is to extend the RPA correlation energy to a 2c formalism that includes the effect of SOC and to efficiently implement the derived theory in the TURBOMOLE program suite. Simultaneously, the 2c RPA correlation energy of diatomic molecules has been calculated by Krause and Klopper using a 2c rCCD approach implemented in a computer program especially written for this purpose.[41]

To arrive at an expression for the 2c RPA correlation energy in the context of DFT that can be efficiently implemented in the RPA module[1,14] of the TURBOMOLE program package, we must first extend the general theory behind RPA to a 2c formalism arriving at the so-called plasmon equation, which describes the 2c RPA correlation energy as a sum over 2c time-dependent Hartree (TDH) excitation energies and 2c TDH excitation energies within the Tamm–Dancoff approximation (TDA).[42] Second, the general 2c non-Hermitian eigenvalue problem for TDH excitation energies is exactly transformed to a 2c Hermitian eigenvalue problem for (Kramers-restricted) closed-shell systems, reducing the dimension of the problem. This transformation is very similar to the approximate one applied in 2c TDDFT for (Kramers-restricted) closed-shell systems.[43,44] Combining all, the plasmon equation is rewritten in terms of the trace of two Hermitian matrices. This formulation of the 2c RPA correlation energy is then efficiently implemented in the same manner as in the 1c case[14] (RI approximation in combination with the representation as an integral over imaginary frequency and evaluation using an exponentially converging Clenshaw–Curtis quadrature), allowing for routine treatments of large systems.

The presented theory is fully operational for different 2c approaches (ZORA, X2C, ECPs), since one-electron relativistic potentials in the Hamiltonian do not lead to additional terms contributing to the 2c RPA correlation energy and therefore, all relativistic effects on the 2c RPA correlation energy arise from the corresponding reference-state spinors and their respective energies only. As a result, the derived formalism can also be easily extended to the 4c formalism, based on the Dirac–Coulomb Hamiltonian.

This paper is organized as follows. In section 2, the plasmon equation for the 2c RPA correlation energy is derived. The 2c RPA correlation energy is finally rewritten in terms of the trace of two Hermitian matrices derived from 2c TDH for (Kramers-restricted) closed-shell systems. Details of the implementation in the RPA module of the TURBOMOLE program package are given in section 3. In section 4, the new implementation is applied to the calculation of the ground-state equilibrium distances and harmonic vibrational frequencies of heavy diatomic molecules as well as the relative ground-state energies of the O_h-, D_{4h}-, and C_{5v}-symmetric isomers of Pb_6. The results are then compared to experimental values and other 2c and 1c computational methods. In the Appendix, the plasmon equation for the 4c RPA correlation energy based on the Dirac–Coulomb–Breit Hamiltonian is derived.

2. THEORY

2.1. Two-Component Random Phase Approximation.
Following the derivation presented by Eshuis, Bates, and Furche,[1] the starting point for a 2c RPA that accounts for SOC effects on the ground-state correlation energy is the 2c adiabatic connection Hamiltonian:[45,46]

$$\hat{\mathbf{H}}^\alpha = \hat{T}\mathbf{1} + \hat{\mathbf{V}}^\alpha[\rho] + \alpha\hat{V}_{ee}\mathbf{1} \tag{1}$$

$\hat{T}$ is the 1c kinetic energy operator of the electrons and $\hat{V}_{ee}$ the 1c Coulomb interaction between the electrons, which is scaled by the dimensionless coupling strength parameter α. $\mathbf{1}$ is the

2×2 identity matrix in spin space. The local one-particle potential $\hat{\mathbf{V}}^\alpha[\rho]$ is the common 1c one-particle potential that additionally contains effective one-particle relativistic potentials, in particular, the 2c SOC contribution, which is nondiagonal in spin space. $\hat{\mathbf{V}}^\alpha[\rho]$ constrains that the ground state $|\Psi_0^\alpha\rangle$ yields the interacting ground-state density ρ for all α.[47] $\alpha = 0$ corresponds to the noninteracting Kohn–Sham system, which is described by the 2c Kohn–Sham Slater determinant $|\Psi_0^0\rangle = |\Psi_0^\alpha\rangle|_{\alpha=0}$.

The total interacting ground-state energy is the expectation value of the 2c physical Hamiltonian $\hat{\mathbf{H}}^\alpha|_{\alpha=1}$ of N interacting electrons, with respect to the 2c Kohn–Sham Slater determinant, plus the correlation energy $E_C[\rho]$, which can be expressed by a coupling strength integral[45,46]

$$E_C[\rho] = \int_0^1 d\alpha W_C^\alpha[\rho] \tag{2}$$

with the coupling strength integrand

$$W_C^\alpha[\rho] = \langle\Psi_0^\alpha[\rho]|\hat{V}_{ee}\mathbf{1}|\Psi_0^\alpha[\rho]\rangle - \langle\Psi_0^0[\rho]|\hat{V}_{ee}\mathbf{1}|\Psi_0^0[\rho]\rangle \tag{3}$$

The Coulomb interaction between the electrons can be written introducing 2c electron field operators $\hat{\psi}^\dagger(\vec{r})$ as

$$\hat{V}_{ee} = \frac{1}{2}\int d^3r_1 \int d^3r_2 \frac{\hat{\psi}^\dagger(\vec{r_1})\hat{\psi}^\dagger(\vec{r_2})\hat{\psi}(\vec{r_1})\hat{\psi}(\vec{r_2})}{|\vec{r_1} - \vec{r_2}|}$$

$$= \frac{1}{2}\int d^3r_1 \int d^3r_2 \frac{\hat{\rho}(\vec{r_1})\hat{\rho}(\vec{r_2}) - \delta(\vec{r_1} - \vec{r_2})\hat{\rho}(\vec{r_1})}{|\vec{r_1} - \vec{r_2}|} \tag{4}$$

In the last step, the fermion anticommutation relations were used to factorize the enumerator in the integrand (that is the two-electron density operator with a prefactor of 2) into products of the one-electron density operator $\hat{\rho}(\vec{r}) = \hat{\psi}^\dagger(\vec{r})\hat{\psi}(\vec{r})$. With the density fluctuation operator $\Delta\hat{\rho}(\vec{r}) = \hat{\rho}(\vec{r}) - \rho(\vec{r})$ and the fact that all one-electron terms cancel since the density $\rho(\vec{r})$ is independent of α, we finally get, for the coupling strength integrand (eq 3),

$$W_C^\alpha = \frac{1}{2}\int d^3r_1 \int d^3r_2 \frac{1}{|\vec{r_1} - \vec{r_2}|}$$
$$\times (\langle\Psi_0^\alpha|\Delta\hat{\rho}(\vec{r_1})\mathbf{1}\Delta\hat{\rho}(\vec{r_2})\mathbf{1}|\Psi_0^\alpha\rangle - \langle\Psi_0^0|\Delta\hat{\rho}(\vec{r_1})\mathbf{1}\Delta\hat{\rho}(\vec{r_2})\mathbf{1}|\Psi_0^0\rangle) \tag{5}$$

The expectation value of $\Delta\hat{\rho}(\vec{r_1})\mathbf{1}\Delta\hat{\rho}(\vec{r_2})\mathbf{1}$ (a two-electron operator) can be factorized into products of complex one-electron transition densities

$$\rho_{0n}^\alpha(\vec{r}) = \langle\Psi_0^\alpha|\hat{\rho}(\vec{r})\mathbf{1}|\Psi_n^\alpha\rangle \tag{6}$$

inserting the completeness of the electronic states $|\Psi_n^\alpha\rangle$ ($n = 0$, 1, 2, ...) at any α ($\sum_n|\Psi_n^\alpha\rangle\langle\Psi_n^\alpha| = 1$). The exact correlation energy (eq 2) then reads

$$E_C = \int_0^1 d\alpha \sum_{n\neq0} (E_H[\rho_{0n}^\alpha] - E_H[\rho_{0n}^0]) \tag{7}$$

with the real Hartree energy functional

$$E_H[\rho_{0n}^\alpha] = \frac{1}{2}\int d^3r_1 \int d^3r_2 \frac{\rho_{0n}^\alpha(\vec{r_1})(\rho_{0n}^\alpha(\vec{r_2}))^*}{|\vec{r_1} - \vec{r_2}|} \tag{8}$$

Thus, the exact 2c ground-state correlation energy can entirely be expressed in terms of complex one-electron transition densities, which are accessible from 2c response theory.

These transition densities can be calculated from the response of the time-dependent Kohn–Sham (TDKS) density matrix determined by the general 2c non-Hermitian TDKS eigenvalue problem for excitation energies ω_n^α:[43,44,48,49]

$$
\begin{pmatrix} A^\alpha_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'} & B^\alpha_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'} \\ (B^\alpha_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'})^* & (A^\alpha_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'})^* \end{pmatrix} \begin{pmatrix} X^\alpha_{j\tilde\sigma' b\tilde\tau',n} \\ Y^\alpha_{j\tilde\sigma' b\tilde\tau',n} \end{pmatrix} = \omega_n^\alpha \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X^\alpha_{i\tilde\sigma a\tilde\tau,n} \\ Y^\alpha_{i\tilde\sigma a\tilde\tau,n} \end{pmatrix}
$$
(9)

where the Einstein summation convention is utilized and indices $i, j, \ldots$ are used for occupied, $a, b, \ldots$ for virtual, and $p, q, \ldots$ for general molecular spinors. Greek indices $\tilde\sigma, \tilde\tau, \tilde\sigma', \tilde\tau' \in \{\tilde\alpha, \tilde\beta\}$ refer to 2c time-reversal symmetry-adapted Kramers partners describing $N_{\tilde\alpha}$ moment-up ($\tilde\alpha$) and $N_{\tilde\beta}$ moment-down ($\tilde\beta$) electrons. The total number of orbitals (occupied plus virtual) is $M_{\tilde\alpha} = N_{\tilde\alpha} + N_{\tilde\alpha}^{\text{virt}}$ and $M_{\tilde\beta} = N_{\tilde\beta} + N_{\tilde\beta}^{\text{virt}}$. The (de)excitation vectors $X^\alpha_{i\tilde\sigma a\tilde\tau,n}$ and $Y^\alpha_{i\tilde\sigma a\tilde\tau,n}$ satisfy the normalization constraint for all α:

$$
\begin{pmatrix} X^\alpha_{i\tilde\sigma a\tilde\tau,n} \\ Y^\alpha_{i\tilde\sigma a\tilde\tau,n} \end{pmatrix}^\dagger \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X^\alpha_{i\tilde\sigma a\tilde\tau,n} \\ Y^\alpha_{i\tilde\sigma a\tilde\tau,n} \end{pmatrix} = 1
$$
(10)

Within 2c RPA, which is identical to 2c TDH theory, the complex (Hermitian) orbital rotation Hessians are defined as

$$
A^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'} = (\varepsilon_{a\tilde\tau} - \varepsilon_{i\tilde\sigma})\delta_{ij}\delta_{ab}\delta_{\tilde\sigma\tilde\sigma'}\delta_{\tilde\tau\tilde\tau'} + \alpha\langle\Phi_{i\tilde\sigma}\Phi_{b\tilde\tau}|\Phi_{a\tilde\tau}\Phi_{j\tilde\sigma'}\rangle
$$
(11)

$$
B^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'} = \alpha\langle\Phi_{i\tilde\sigma}\Phi_{j\tilde\sigma'}|\Phi_{a\tilde\tau}\Phi_{b\tilde\tau'}\rangle
$$
(12)

$\varepsilon_{p\tilde\sigma}$ describes the energy of 2c spinor $\Phi_{p\tilde\sigma}$ and δ_{pq} is the Kronecker delta. The second term in eq 11 is the Coulomb matrix element in Dirac notation. Since only one-electron relativistic potentials are included in $\hat{V}^\alpha[\rho]$ in the Hamiltonian (eq 1) accounting for SOC, they do not respond to a TD external perturbation. As a result, there is no additional SOC contribution to the orbital rotation Hessians and SOC effects on excitations arise via the reference-state spinors and their energies only. In the 1c limit, moment-up/moment-down ($\tilde\alpha/\tilde\beta$) electrons become ordinary spin-up/spin-down (α/β) electrons. As a result, $\mathbf{A}^{\alpha\text{RPA}}$ and $\mathbf{B}^{\alpha\text{RPA}}$ are real and the MOs $\Phi_{p\sigma}$ are eigenfunctions of $\hat{S}_z$. With the complex first-order RPA/TDH transition density

$$
\rho^{\alpha\text{RPA}(1)}_{0n}(\omega_n^\alpha, \vec{r}) = \sum_{\tilde\sigma\tilde\tau}\sum_{i=1}^{N_{\tilde\sigma}}\sum_{a=N_{\tilde\tau}+1}^{M_{\tilde\tau}} X^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}(\omega_n^\alpha)\Phi^\dagger_{i\tilde\sigma}(\vec{r})\Phi_{a\tilde\tau}(\vec{r}) \\ + Y^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}(\omega_n^\alpha)\Phi^\dagger_{a\tilde\tau}(\vec{r})\Phi_{i\tilde\sigma}(\vec{r})
$$
(13)

and eqs 7 and 8, the correlation energy reads

$$
E_C^{\text{RPA}} = \frac{1}{2}\int_0^1 d\alpha \sum_{n\neq 0}\sum_{\tilde\sigma\tilde\tau}\sum_{i=1}^{N_{\tilde\sigma}}\sum_{a=N_{\tilde\tau}+1}^{M_{\tilde\tau}}\sum_{\tilde\sigma'\tilde\tau'}\sum_{j=1}^{N_{\tilde\sigma'}}\sum_{b=N_{\tilde\tau'}+1}^{M_{\tilde\tau'}}
$$

$$
+ [(X^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}(\omega_n^\alpha))^* X^{\alpha\text{RPA}}_{j\tilde\sigma' b\tilde\tau',n}(\omega_n^\alpha) - \delta_{ij}\delta_{ab}\delta_{\tilde\sigma\tilde\sigma'}\delta_{\tilde\tau\tilde\tau'}]\langle\Phi_{i\tilde\sigma}\Phi_{b\tilde\tau}|\Phi_{a\tilde\tau}\Phi_{j\tilde\sigma'}\rangle
$$

$$
+ [(Y^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}(\omega_n^\alpha))^* X^{\alpha\text{RPA}}_{j\tilde\sigma' b\tilde\tau',n}(\omega_n^\alpha) - \delta_{ij}\delta_{ab}\delta_{\tilde\sigma\tilde\sigma'}\delta_{\tilde\tau\tilde\tau'}]\langle\Phi_{a\tilde\tau}\Phi_{b\tilde\tau}|\Phi_{i\tilde\sigma}\Phi_{j\tilde\sigma'}\rangle
$$

$$
+ [(X^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}(\omega_n^\alpha))^* Y^{\alpha\text{RPA}}_{j\tilde\sigma' b\tilde\tau',n}(\omega_n^\alpha) - \delta_{ij}\delta_{ab}\delta_{\tilde\sigma\tilde\sigma'}\delta_{\tilde\tau\tilde\tau'}]\langle\Phi_{i\tilde\sigma}\Phi_{j\tilde\sigma'}|\Phi_{a\tilde\tau}\Phi_{b\tilde\tau'}\rangle
$$

$$
+ [(Y^{\alpha\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}(\omega_n^\alpha))^* Y^{\alpha\text{RPA}}_{j\tilde\sigma' b\tilde\tau',n}(\omega_n^\alpha) - \delta_{ij}\delta_{ab}\delta_{\tilde\sigma\tilde\sigma'}\delta_{\tilde\tau\tilde\tau'}]\langle\Phi_{a\tilde\tau}\Phi_{j\tilde\sigma'}|\Phi_{i\tilde\sigma}\Phi_{b\tilde\tau'}\rangle
$$
(14)

Applying the Hellmann–Feynman theorem[50] to eq 9 and comparing the result to eq 14, it follows that

$$
\frac{d\omega_n^{\alpha\text{RPA}}}{d\alpha} = 2E_H[\rho^{\alpha\text{RPA}(1)}_{0n}]
$$
(15)

which leads to the expression

$$
E_C^{\text{RPA}} = \frac{1}{2}\int_0^1 d\alpha \sum_n \left(\frac{d\omega_n^{\alpha\text{RPA}}}{d\alpha} - \frac{d\omega_n^{\alpha\text{RPA}}}{d\alpha}\bigg|_{\alpha=0}\right)
$$
(16)

for the correlation energy within RPA. Carrying out the coupling strength integration analytically, we finally get the plasmon formula:

$$
E_C^{\text{RPA}} = \frac{1}{2}\sum_n (\omega_n^{\text{RPA}} - \omega_n^{\text{TDA RPA}})
$$
(17)

This result is analogous to the 1c expression but with the respective excitation energies calculated within a 2c formalism; ω_n^{RPA} represents the 2c RPA/TDH excitation energies at full coupling, and $\omega_n^{\text{TDA RPA}}$ represents the 2c RPA/TDH excitation energies within the TDA.[42]

Equation 17 can be easily extended to the fully relativistic 4c formalism based on the Dirac–Coulomb Hamiltonian by calculating the respective excitation energies within a 4c theory. However, if the Dirac–Coulomb–Breit Hamiltonian (which is the expansion of the quantum-electrodynamic (QED) Hamiltonian up to $O(1/c^2)$, with c being the speed of light) is used, the derivation of the RPA correlation energy gets more involved since the interaction between the electrons $\hat{V}_{ee}$ contains additional terms, that account for retardation effects and magnetic interactions besides the bare instantaneous Coulomb interaction. As shown in the Appendix, one again arrives at eq 17 with the respective excitation energies calculated within a 4c theory based on the Dirac–Coulomb–Breit Hamiltonian (the orbital rotation Hessians in eqs 11 and 12 contain additional two-electron terms).

2.2. Two-Component Time-Dependent Hartree Theory. To arrive at an expression for E_C^{RPA} that builds the foundation for an efficient implementation,[1,14] the challenge is to transform eq 9 (for $\alpha = 1$) to a Hermitian eigenvalue problem:[11]

$$
\Omega^{\text{RPA}}_{i\tilde\sigma a\tilde\tau j\tilde\sigma' b\tilde\tau'}(X+Y)'^{\text{RPA}}_{j\tilde\sigma' b\tilde\tau',n} = (\omega_n^{\text{RPA}})^2(X+Y)'^{\text{RPA}}_{i\tilde\sigma a\tilde\tau,n}
$$
(18)

With this, eq 17 can be rewritten as the (real) trace of two Hermitian matrices

$$
E_C^{\text{RPA}} = \frac{1}{2}\text{tr}((\mathbf{\Omega}^{\text{RPA}})^{1/2} - \mathbf{A}^{\text{RPA}})
$$
(19)

and implemented following the algorithm presented by Eshuis, Yarkony, and Furche in ref 14. Within a 1c RPA/TDH formalism, the computation of $\mathbf{\Omega}^{\text{RPA}}$ from eq 9 is straightforward since $\mathbf{A}^{\text{RPA}}$ and $\mathbf{B}^{\text{RPA}}$ are real and their difference is diagonal. In general, this is not true for the 2c case and, at first sight, it seems impossible to set up $\mathbf{\Omega}^{\text{RPA}}$. However, following the derivations presented by Wang et al.[43] and Peng et al.[44] in the case of 2c (Kramers-restricted) closed-shell TDDFT that arrive at eq 18, which is approximate in the case of 2c TDDFT, it is shown in the following that this equation is exact in the case of 2c RPA/TDH and can be used to efficiently evaluate E_C^{RPA} (eq 19) for (Kramers-restricted) closed-shell systems.

The general 2c non-Hermitian TDKS eigenvalue problem (eq 9) can be written as two coupled equations, inserting

the expressions for the orbital rotation Hessians from eqs 11 and 12:

$$X_{i\tilde{\sigma}a\tilde{\tau},n}^{\mathrm{RPA}}(\omega_n) = \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N_{\tilde{\sigma}'}}\sum_{b=N_{\tilde{\tau}'}+1}^{M_{\tilde{\tau}'}}\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}|\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}}\rangle X_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}(\omega_n) + \langle\Phi_{i\tilde{\sigma}}\Phi_{j\tilde{\sigma}}|\Phi_{a\tilde{\tau}}\Phi_{b\tilde{\tau}}\rangle Y_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}(\omega_n)}{\omega_n^{\mathrm{RPA}} - (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})} \tag{20}$$

$$Y_{i\tilde{\sigma}a\tilde{\tau},n}^{\mathrm{RPA}}(\omega_n) = \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N_{\tilde{\sigma}'}}\sum_{b=N_{\tilde{\tau}'}+1}^{M_{\tilde{\tau}'}}\langle\Phi_{a\tilde{\tau}}\Phi_{b\tilde{\tau}}|\Phi_{i\tilde{\sigma}}\Phi_{j\tilde{\sigma}}\rangle X_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}(\omega_n) + \langle\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}}|\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}\rangle Y_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}(\omega_n)}{-\omega_n^{\mathrm{RPA}} - (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})} \tag{21}$$

In the next step, time-reversal symmetry is exploited. For a (Kramers-restricted) closed-shell system $N_{\tilde{\alpha}} = N_{\tilde{\beta}} = N/2$ and $\varepsilon_{p\tilde{\alpha}} = \varepsilon_{p\tilde{\beta}}$, since the Kramers partners $\Phi_{p\tilde{\alpha}}$ and $\Phi_{p\tilde{\beta}}$ are either both occupied or unoccupied. Utilizing the Kramers identities $\Phi_{p\tilde{\beta}}^{\dagger}\Phi_{q\tilde{\beta}} = \Phi_{q\tilde{\alpha}}^{\dagger}\Phi_{p\tilde{\alpha}}$ and $\Phi_{p\tilde{\beta}}^{\dagger}\Phi_{q\tilde{\alpha}} = -\Phi_{q\tilde{\beta}}^{\dagger}\Phi_{p\tilde{\alpha}}$ for interchanging indices $j\tilde{\sigma}'$ and $b\tilde{\tau}'$, eqs 20 and 21 can be rewritten as

$$X_{i\tilde{\sigma}a\tilde{\tau},n}^{\mathrm{RPA}}(\omega_n)$$
$$= \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N/2}\sum_{b=(N/2)+1}^{M/2}\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}|\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}}\rangle(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}}{\omega_n^{\mathrm{RPA}} - (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})} \tag{22}$$

$$Y_{i\tilde{\sigma}a\tilde{\tau},n}^{\mathrm{RPA}}(\omega_n)$$
$$= \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N/2}\sum_{b=(N/2)+1}^{M/2}\langle\Phi_{a\tilde{\tau}}\Phi_{b\tilde{\tau}}|\Phi_{i\tilde{\sigma}}\Phi_{j\tilde{\sigma}}\rangle(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}}{-\omega_n^{\mathrm{RPA}} - (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})} \tag{23}$$

with

$$(X+Y)_{j\tilde{\sigma}'b\tilde{\sigma}',n}^{\mathrm{RPA}} = X_{j\tilde{\sigma}'b\tilde{\sigma}',n}^{\mathrm{RPA}}(\omega_n) + Y_{j\tilde{\tau}'b\tilde{\tau}',n}^{\mathrm{RPA}}(\omega_n) \quad \text{for } \tilde{\sigma}' \neq \tilde{\tau}' \tag{24}$$

$$(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}} = X_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}(\omega_n) - Y_{j\tilde{\tau}'b\tilde{\sigma}',n}^{\mathrm{RPA}}(\omega_n) \quad \text{for } \tilde{\sigma}' \neq \tilde{\tau}' \tag{25}$$

Using the Kramers identities again for the interchange of indices $i\tilde{\sigma}$ and $a\tilde{\tau}$, eq 23 becomes

$$Y_{i\tilde{\tau}a\tilde{\tau},n}^{\mathrm{RPA}}(\omega_n) = \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N/2}\sum_{b=(N/2)+1}^{M/2}\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}|\Phi_{a\tilde{\sigma}}\Phi_{j\tilde{\sigma}}\rangle(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}}{-\omega_n^{\mathrm{RPA}} - (\varepsilon_{a\tilde{\sigma}} - \varepsilon_{i\tilde{\sigma}})}$$
$$\text{for } \tilde{\sigma} \neq \tilde{\tau} \tag{26}$$

$$Y_{i\tilde{\tau}a\tilde{\sigma},n}^{\mathrm{RPA}}(\omega_n) = \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N/2}\sum_{b=(N/2)+1}^{M/2}\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}|\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}}\rangle(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}}{\omega_n^{\mathrm{RPA}} + (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})}$$
$$\text{for } \tilde{\sigma} \neq \tilde{\tau} \tag{27}$$

Inserting eqs 22 and 26 into eq 24 and eqs 22 and 27 into eq 25 gives

$$(X+Y)_{i\tilde{\sigma}a\tilde{\tau},n}^{\mathrm{RPA}}$$
$$= \frac{\sum_{\tilde{\sigma}'\tilde{\tau}'}\sum_{j=1}^{N/2}\sum_{b=(N/2)+1}^{M/2}2(\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}|\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}}\rangle(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}}}{(\omega_n^{\mathrm{RPA}})^2 - (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})^2} \tag{28}$$

As a result, eq 18 is obtained with the Hermitian

$$\Omega_{i\tilde{\sigma}a\tilde{\tau}j\tilde{\sigma}'b\tilde{\tau}'}^{\mathrm{RPA}} = (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})^2\delta_{ij}\delta_{ab}\delta_{\tilde{\sigma}\tilde{\sigma}'}\delta_{\tilde{\tau}\tilde{\tau}'}$$
$$+ 2\sqrt{\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}}}\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}}|\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}'}\rangle\sqrt{\varepsilon_{b\tilde{\tau}'} - \varepsilon_{j\tilde{\sigma}'}} \tag{29}$$

and

$$(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{\mathrm{RPA}} = \sqrt{\varepsilon_{b\tilde{\tau}'} - \varepsilon_{j\tilde{\sigma}'}}(X+Y)_{j\tilde{\sigma}'b\tilde{\tau}',n}^{'\mathrm{RPA}}$$

As mentioned previously, the transformation of eq 9 to eq 18 is exact in the case of 2c (Kramers-restricted) closed-shell RPA/TDH, as opposed to 2c closed-shell TDDFT,[43,44] since no (polarized) exchange-correlation potential is present that would lead to a first-order induced internal magnetic field breaking time-reversal symmetry. For open-shell systems, it is not possible to apply an analogous transformation that arrives at eq 18, neither in the case of 2c TDDFT nor 2c RPA/TDH. However, eq 18 can be extended to the 4c formalism based on the Dirac−Coulomb Hamiltonian simply by replacing all 2c spinors by 4c ones.[44,51−53]

3. EFFICIENT EVALUATION OF THE CORRELATION ENERGY WITHIN THE RANDOM PHASE APPROXIMATION AND IMPLEMENTATION

In section 2.2, the 2c RPA correlation energy was rewritten in terms of the square root of $\mathbf{\Omega}^{\mathrm{RPA}}$ (eq 19) for (Kramers-restricted) closed-shell systems. To avoid the $O(N^6)$-scaling full diagonalization of $\mathbf{\Omega}^{\mathrm{RPA}}$, where N characterizes the system size, the technique presented by Eshuis et al.[1,14] is followed using the representation of eq 19 as an integral over imaginary frequency[16] in combination with the RI approximation.[14,54−58] The latter has already successfully been applied in 2c DFT,[38] 2c TDDFT,[40] and 2c MP2[39] implementations.

Utilizing the RI approximation the complex two-electron matrix element in eq 29 can be factorized (in Mulliken notation) as

$$(\Phi_{i\tilde{\sigma}}\Phi_{a\tilde{\tau}}|\Phi_{b\tilde{\tau}}\Phi_{j\tilde{\sigma}'})_{\mathrm{RI}} = \sum_{P,R=1}^{N_{\mathrm{BF,aux}}}(\Phi_{i\tilde{\sigma}}\Phi_{a\tilde{\tau}}|\chi_P)(\chi_P|\chi_R)^{-1}(\chi_R|\Phi_{b\tilde{\tau}}\Phi_{j\tilde{\sigma}'})$$
$$= \sum_{T=1}^{N_{\mathrm{BF,aux}}}\left(\sum_{P=1}^{N_{\mathrm{BF,aux}}}(\Phi_{i\tilde{\sigma}}\Phi_{a\tilde{\tau}}|\chi_P)L_{PT}^{-1}\right)\left(\sum_{R=1}^{N_{\mathrm{BF,aux}}}L_{TR}^{-1}(\chi_R|\Phi_{b\tilde{\tau}}\Phi_{j\tilde{\sigma}'})\right)$$
$$= \sum_{T=1}^{N_{\mathrm{BF,aux}}}S_{i\tilde{\sigma}a\tilde{\tau},T}S_{T,b\tilde{\tau}'j\tilde{\sigma}'} \tag{30}$$

where χ_P are common (1c) real atom-centered auxiliary basis functions and L_{PT} is calculated by Cholesky decomposition of the two-electron integrals $(\chi_P|\chi_R)$. The number of auxiliary basis functions $N_{BF,aux}$ depends only linearly on the system size N, which makes it much more efficient to consider the two-electron matrix element within the RI approximation instead of using the full matrix element.

To avoid the construction of four-index quantities entirely, both $(\mathbf{\Omega}^{RPA})^{1/2}$ and $\mathbf{A}^{RPA}$ in eq 19 are evaluated as an integral over imaginary frequency (see ref 14), inspired by the work of Hale et al.,[16] where the respective matrices are allowed to be complex in general. The final expression for the 2c RPA correlation energy within the RI approximation of (Kramers-restricted) closed-shell systems is

$$E_C^{RPA} = \int_{-\infty}^{\infty} \frac{d\nu}{2\pi} F_C(\nu) \tag{31}$$

with the real integrand

$$F_C(\nu) = \frac{1}{2}\text{tr}(\ln(\mathbf{1} + \mathbf{Q}(\nu)) - \mathbf{Q}(\nu)) \tag{32}$$

The matrix $\mathbf{Q}(\nu)$ is in auxiliary basis ($N_{BF,aux} \times N_{BF,aux}$) and reads

$$Q_{PR}(\nu) = \sum_{\bar{\sigma}\bar{\sigma}'} \sum_{\bar{\tau}\bar{\tau}'} \sum_{i,j=1}^{N/2} \sum_{a,b=(N/2)+1}^{M/2} 2 S_{P,b\bar{\tau}'j\bar{\sigma}'} G_{i\bar{\sigma}a\bar{\tau}j\bar{\sigma}'b\bar{\tau}'}(\nu) S_{i\bar{\sigma}a\bar{\tau},R} \tag{33}$$

with the real

$$G_{i\bar{\sigma}a\bar{\tau}j\bar{\sigma}'b\bar{\tau}'}(\nu) = \frac{(\varepsilon_{a\bar{\tau}} - \varepsilon_{i\bar{\sigma}})}{(\varepsilon_{a\bar{\tau}} - \varepsilon_{i\bar{\sigma}})^2 + \nu^2}\delta_{ij}\delta_{ab}\delta_{\bar{\sigma}\bar{\sigma}'}\delta_{\bar{\tau}\bar{\tau}'} \tag{34}$$

Since the summation over $i\bar{\sigma}$ and $j\bar{\sigma}'$ ($a\bar{\tau}$ and $b\bar{\tau}'$) in eq 33 runs over all occupied (virtual) orbitals and $(\Phi_{i\bar{\sigma}}\Phi_{a\bar{\tau}}|\Phi_{b\bar{\tau}'}\Phi_{j\bar{\sigma}'})_{RI}$ (eq 30) is Hermitian, $Q_{PR}(\nu)$ is real for all P and R and can thus be rewritten in terms of real and imaginary parts as

$$Q_{PR}(\nu) = \sum_{\bar{\sigma}\bar{\sigma}'} \sum_{\bar{\tau}\bar{\tau}'} \sum_{i,j=1}^{N/2} \sum_{a,b=(N/2)+1}^{M/2} 2[\Re(S_{P,b\bar{\tau}'j\bar{\sigma}'}) G_{i\bar{\sigma}a\bar{\tau}j\bar{\sigma}'b\bar{\tau}'}(\nu) \Re(S_{i\bar{\sigma}a\bar{\tau},R})$$
$$+ \Im(S_{P,b\bar{\tau}'j\bar{\sigma}'}) G_{i\bar{\sigma}a\bar{\tau}j\bar{\sigma}'b\bar{\tau}'}(\nu) \Im(S_{i\bar{\sigma}a\bar{\tau},R})] \tag{35}$$

The final result for the 2c RPA correlation energy of (Kramers-restricted) closed-shell systems (eqs 31, 32, 35, and 34) is analogous to the 1c expression[1,14] and has the correct 1c limit. Again, the result can be easily extended to the 4c formalism, based on the Dirac−Coulomb Hamiltonian by replacing all 2c spinors by 4c ones.

For the sake of completeness, the analytical structure of the 2c RPA correlation energy is obtained using the spectral representation of $\mathbf{\Omega}^{RPA}$ in the same manner as in the 1c case:

$$E_C^{RPA} = \int_{-\infty}^{\infty} \frac{d\nu}{2\pi} \frac{1}{2} \sum_{\bar{\sigma}\bar{\tau}} \sum_{i=1}^{N/2} \sum_{a=(N/2)+1}^{M/2} \left[\ln\left(1 + \frac{\omega_{(i\bar{\sigma}a\bar{\tau})}^{RPA} - (\varepsilon_{a\bar{\tau}} - \varepsilon_{i\bar{\sigma}})^2}{\nu^2 + (\varepsilon_{a\bar{\tau}} - \varepsilon_{i\bar{\sigma}})^2}\right) \right.$$
$$\left. - \frac{\Omega_{i\bar{\sigma}a\bar{\tau}i\bar{\sigma}a\bar{\tau}}^{RPA} - (\varepsilon_{a\bar{\tau}} - \varepsilon_{i\bar{\sigma}})^2}{\nu^2 + (\varepsilon_{a\bar{\tau}} - \varepsilon_{i\bar{\sigma}})^2} \right] \tag{36}$$

Equations 31, 32, 35, and 34 were implemented in the RIRPA module[1,14] of the TURBOMOLE program suite, mainly by extending the existing 1c routines to the 2c formalism. As in the 1c treatment, a Clenshaw−Curtis quadrature is used to evaluate eq 31 efficiently.[14,17] 2c computations are more demanding, with regard to computation time and required memory, than 1c ones. Within the RIRPA module, both scale as

$O(N^4 \log N)$ but with an additional prefactor of 4 (8) for the 2c implementation, compared to the 1c open-shell (closed-shell) variant.

It was ensured that the 2c RPA correlation energy is invariant under rotations in spin space and that the correct 1c limit is always obtained. Furthermore, the 2c rCCD[41] (without exchange) yields the same results for all systems tested.

It is noted, in passing, that it is straightforward to generalize the so-called "beyond-RPA corrections" to the RPA correlation energy, such as semilocal density functional corrections (RPA+),[59] the promising new approximate exchange kernel (AXK),[60] and the popular second-order screened exchange (SOSEX),[61,62] to a 2c formalism. In particular, as shown in ref 14, the RI approximation to the cluster amplitudes can be identified as an integral over imaginary frequency, which could also be used to evaluate 2c SOSEX corrections.

4. APPLICATIONS

Computational Details. All ground-state structures of the Pb_6 (O_h, triplet occupation; D_{4h}, singlet occupation; C_{5v}, singlet occupation) isomers were optimized under symmetry constraints using 1c DFT and the GGA functional of Perdew, Burke, and Ernzerhof (PBE),[63] in combination with a doubly polarized quadruple-ζ valence basis set (dhf-QZVPP-2c).[64] The Dirac−Hartree−Fock (dhf) bases are optimized for the use with the dhf-ECPs, which account for scalar relativistic effects in 1c calculations and additionally for SOC effects in 2c calculations. For Pb, a pseudo-potential (dhf-ECP-60),[33] covering the inner 60 electrons, was used. The coordinates of the Pb_6 isomers are given in Tables II−IV in the Supporting Information.

Ground-state energies of Pb_6 and diatomic molecules were computed at both the 2c and 1c levels, using the GGA functional PBE,[63] Becke's three-parameter hybrid functional with Lee−Yang−Parr correlation (B3LYP),[65] HF theory, MP2 theory based on HF, and RPA based on PBE orbitals/spinors and their respective energies. For Pb_6 the meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria (TPSS)[66] was additionally used. dhf-QZVPP-2c basis sets were applied in all calculations, which are sufficiently large for most applications at the (correlated) MP2 and RPA level.[67] For I and Ag, pseudo-potentials (dhf-ECP-28)[32,34] covering the inner 28 electrons were used; for Cs, a pseudo-potential (dhf-ECP-46)[35] covering the inner 46 electrons was used; and for Tl, Au, and At, pseudo-potentials (dhf-ECP-60)[32−34] covering the inner 60 electrons were used.

In all calculations using pure density functionals, the RI approximation[54] was employed for the Coulomb integrals and in calculations at the B3LYP and HF level additionally for the exchange integrals.[68] The applied auxiliary basis sets[69] are suited for bases optimized for dhf-ECPs.[70] At the (correlated) MP2 and RPA level, the respective 1c MP2-optimized (decontracted) auxiliary basis sets (def2-QZVPP) were used.[58,71−73]

Reference-state energies and density matrices were converged to 10^{-10} a.u. At the DFT level, fine quadrature grids of size 5 were employed.[74] In MP2 and RPA calculations, all orbitals/spinors with energies below 3 a.u. were excluded from the correlation treatment. In the RPA procedure, the Clenshaw−Curtis quadrature[14] was performed using at least 200 grid points. For some (small-gap) systems, the number of grid points was increased—especially in cases where the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied

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Table 1. Scalar Relativistic (1c) and Two-Component (2c) Ground-State Equilibrium Distances and Harmonic Vibrational Frequencies of Six Diatomic Molecules Using Different Methods[a]

Molecule	Method	Equilibrium Distance (pm)			Vibrational Frequency (cm^{-1})		
		1c	2c	Exp.[b]	1c	2c	Exp.[b]
I_2	RPA	268.3	269.7	266.6	213	206	215
	MP2	262.9	264.1		238	230	
	HF	266.0	267.3		237	229	
	B3LYP	269.6	271.7		212	201	
	PBE	268.7	270.7		213	202	
HI	RPA	160.7	160.9	160.9	2312	2294	2309
	MP2	159.3	159.6		2413	2396	
	HF	159.9	160.1		2449	2431	
	B3LYP	161.7	162.0		2291	2267	
	PBE	162.5	162.9		2248	2224	
HCs	RPA	248.1	248.0	249.4	871	872	891
	MP2	247.1	247.0		912	912	
	HF	258.6	258.5		854	855	
	B3LYP	250.4	250.3		875	876	
	PBE	248.5	248.4		869	870	
TlH	RPA	190.6	188.6	187.0	1353	1359	1391
	MP2	188.2	185.9		1420	1435	
	HF	189.5	186.7		1422	1451	
	B3LYP	191.7	189.2		1344	1357	
	PBE	192.5	190.1		1318	1327	
AgH	RPA	160.1	160.2	161.8	1779	1776	1760
	MP2	156.3	156.4		1939	1936	
	HF	169.7	169.8		1608	1606	
	B3LYP	161.6	161.7		1776	1773	
	PBE	160.4	160.5		1806	1803	
AuH	RPA	151.8	151.7	152.4	2296	2304	2305
	MP2	148.4	148.3		2527	2534	
	HF	157.2	156.9		2083	2101	
	B3LYP	154.0	154.0		2230	2238	
	PBE	153.6	153.6		2255	2259	

[a]All calculated values were obtained using dhf-QZVPP-2c basis sets and dhf-ecp-2c spin-orbit effective core potentials (ECPs). [b]Experimental values are taken from ref 75.

molecular orbital (LUMO) is decreased due to SOC—to ensure that the estimated error in the correlation energy (sensitivity parameter) due to the numerical integration is always smaller than 10^{-8} a.u. In all 2c PBE reference-state calculations, it was checked that the noncollinear spin density is zero to ensure the presented 2c RPA (Kramers-restricted) closed-shell implementation is applicable.

The equilibrium distances and vibrational frequencies of diatomic molecules were calculated using a polynomial (degree 9) least-squares fit by singular value decomposition based on 60 single-point ground-state energy calculations around the estimated equilibrium distance. The interatomic distance was increased by 0.01 a.u. between two single-point calculations.

4.1. Equilibrium Distances and Vibrational Frequencies of Heavy Diatomic Molecules. The ground-state equilibrium distances and harmonic vibrational frequencies of the closed-shell species I_2, HI, HCs, TlH, AgH, AuH, and At_2 were calculated at both the 2c and 1c levels, using RPA, MP2, HF, B3LYP, and PBE, in combination with QZVPP basis sets, and compared to experimental data.[75] Results are shown in Table 1.

Deviations among the different 1c computational methods (equilibrium distances, <14 pm; vibrational frequencies, <445 cm^{-1}) are larger than the absolute errors, with respect to the experiment (equilibrium distances, <10 pm, vibrational frequencies, <225 cm^{-1}), and are much larger than the effect of SOC on equilibrium distances and vibrational frequencies. The inclusion of SOC changes equilibrium distances by <3 pm and vibrational frequencies by <30 cm^{-1}. All of the studied computational methods show similar trends going from the 1c version to their respective 2c versions. The 2c and 1c RPA, MP2, and PBE results of HI, AgH, and AuH are in reasonable agreement (equilibrium distances within 1.3 pm, vibrational frequencies within 70 cm^{-1}) with the values obtained by Krause and Klopper, using rCCD-based RPA, MP2, and PBE in combination with the all-electron X2C approach and decontracted relativistic atomic-natural-orbital basis sets.[41]

In case of the homonuclear I_2 and the heteronuclear HI, the inclusion of SOC leads to elongations of equilibrium distances (for I_2, 1.2−2.1 pm; for HI, 0.2−0.4 pm) while the vibrational frequencies are reduced (for I_2, 7−11 cm^{-1}; for HI, 17−24 cm^{-1}), meaning that the bonds are weakened.

In contrast, for both HCs and TlH, going from the 1c formalism to the 2c formalism leads to shorter equilibrium distances (for HCs, ca. 0.1 pm; for TlH, 1.5−2.8 pm) and higher vibrational frequencies (for HCs, ca. 1 cm^{-1}; for TlH, 9−29 cm^{-1}).

In case of AgH, effects are very small (equilibrium distance is elongated by ca. 0.1 pm, vibrational frequency reduced by 2−3 cm^{-1}) and for AuH, the equilibrium distance is shortened (by up to 0.3 pm) and the vibrational frequency is increased (4−18 cm^{-1}) when SOC is included. For AgH, trends in both equilibrium distances and vibrational frequencies when going from 1c methods to 2c methods are somehow contrary to those observed by Krause and Klopper (RPA, MP2, and PBE);[41] however, the deviations are very small. These disagreements may be traced back to the use of different basis sets and different relativistic approaches.

In a statistical analysis of the results presented in this section (see Table 2), RPA performs best, in terms of the mean absolute

Table 2. Performance of Ground-State Equilibrium Distances and Harmonic Vibrational Frequencies on Six Diatomic Molecules Using Different Scalar Relativistic (1c) and Two-Component (2c) Methods[a]

Method[b]	Equilibrium Distance (pm)		Vibrational Frequency (cm^{-1})	
	1c	2c	1c	2c
RPA				
MAE	1.5	1.4	15	15
SD	2.0	1.9	21	20
MaxAE	3.6	3.1	38	32
MP2				
MAE	3.1	2.8	96	96
SD	3.7	3.5	137	137
MaxAE	5.5	5.4	222	229
HF				
MAE	4.3	3.9	101	99
SD	6.0	5.8	138	131
MaxAE	9.2	9.1	222	204
B3LYP				
MAE	1.9	1.8	29	31
SD	2.7	2.7	42	40
MaxAE	4.7	5.1	75	67
PBE				
MAE	2.1	2.1	42	45
SD	2.9	2.6	53	57
MaxAE	5.5	4.1	73	85

[a]All calculated values were obtained using dhf-QZVPP-2c basis sets and dhf-ecp-2c spin-orbit effective core potentials (ECPs). [b]MAE denotes the mean absolute error, SD the standard deviation, and MaxAE the maximum absolute error.

error (MAE), the standard deviation (SD), and the maximum absolute error (MaxAE), with respect to the experimental values. On average, RPA, HF, and (hybrid) DFT overestimate equilibrium distances and underestimate vibrational frequencies, whereas MP2 underestimates equilibrium distances and overestimates vibrational frequencies. RPA has a MAE (standard deviation, SD) of 1.5 pm (2.0 pm) in the case of equilibrium distances and 15 cm^{-1} (20 cm^{-1}) in the case of vibrational frequencies. The MaxAE in the equilibrium distances occurs for I$_2$ and TlH (ca. 3.5 pm) and in vibrational frequencies for TlH (ca. 35 cm^{-1}). RPA performs better than B3LYP and PBE,

which have a MAE (SD) of ca. 2.0 pm (2.7 pm) in the case of equilibrium distances and ca. 40 cm^{-1} (50 cm^{-1}) in the case of vibrational frequencies. For both methods, the MaxAE in the equilibrium distances occurs for I$_2$ and TlH (ca. 5 pm). In the case of vibrational frequencies, the B3LYP absolute error is largest for AuH and the PBE absolute error is largest for HI and TlH (ca. 80 cm^{-1}). RPA (and also B3LYP and PBE) outperforms both MP2 and HF, with respect to all statistical parameters. The MAE (SD) of MP2 is ca. 3.0 pm (3.5 pm) and that of HF ca. 4.0 pm (6.0 pm) in the case of equilibrium distances. For both methods, the MAE (SD) of the vibrational frequencies is ca. 100 cm^{-1} (140 cm^{-1}). The MP2 MaxAE in equilibrium distances occurs for AgH (5.5 pm) and the HF MaxAE occurs for HCs (9.1 pm). For both MP2 and HF, the absolute error in vibrational frequencies is largest for AuH (220 cm^{-1}).

Taking into account SOC slightly improves all statistical parameters for all methods, with regard to the equilibrium distances. Both the MAE and the SD are reduced by ca. 0.2 pm, on average. The MaxAE also decreases by 0.3 pm, on average. However, the picture is more diffuse for the vibrational frequencies, which are more sensitive. The MAE remains constant, whereas the SD is reduced by ca. 1 cm^{-1} and the MaxAE by ca. 3 cm^{-1}, on average.

In the case of At$_2$, the effect of SOC on equilibrium distances (increase by 10.4 pm for MP2, up to 16.6 pm for B3LYP) and vibrational frequencies (decrease by 35 cm^{-1} for MP2, up to 44 cm^{-1} for PBE and B3LYP) is larger than the deviations among the different 1c computational methods (equilibrium distances, ≤7.3 pm; vibrational frequencies, <20 cm^{-1}), see Table I in the Supporting Information. For RPA, the equilibrium distance increases by 13.0 pm and the vibrational frequency decreases by 38 cm^{-1}, which, again, is consistent with the other methods. Unfortunately, no experimental values are available; thus, At$_2$ is excluded from the statistics above.

Overall, the errors in equilibrium distances and vibrational frequencies, with respect to the experiment using (1c and 2c) RPA, are smaller than those obtained using the other methods (B3LYP, PBE, MP2, HF). The differences in equilibrium distances and vibrational frequencies when including SOC within RPA are in reasonable agreement with those obtained from other methods.

4.2. Relative Energies of the O_h-, D_{4h}-, and C_{5v}-Symmetric Isomers of Pb$_6$. The relative ground-state energies of the O_h-, D_{4h}-, and C_{5v}-symmetric isomers of Pb$_6$ were calculated at both the 2c and 1c level using RPA, HF, B3LYP, TPSS, and PBE in combination with the QZVPP basis set. Results are shown in Table 3. The coordinates of the optimized structures using 1c DFT at the PBE/QZVPP level are given in Tables II−IV in the Supporting Information.

Recent DFT studies have shown that Pb$_6$ exhibits a Jahn−Teller distortion in the 1c case and thus forms the D_{4h}-symmetric isomer as a minimum-energy structure, which is lower in energy than the O_h-symmetric structure by 77.7 kJ mol^{-1} (105.0 kJ mol^{-1}) at the 1c pure (hybrid) DFT level.[38] The ground-state degeneracy of the O_h-symmetric isomer is lifted by SOC. As a consequence, in the 2c DFT case, the highly symmetric O_h isomer is no longer a Jahn−Teller case (distortion does not lead to an energy gain) and thus the clear preference of D_{4h} symmetry is removed.[38,76,77] In the work of Armbruster et al.,[38] the relative energy of the D_{4h}-symmetric structure is higher in energy than the O_h-symmetric one by 5.5 kJ mol^{-1} (15.6 kJ mol^{-1}) at the 2c pure (hybrid) DFT level.

Table 3. Scalar Relativistic (1c) and Two-Component (2c) Relative Ground-State Energies of the O_h-, D_{4h}-, and C_{5v}-Symmetric Isomers of Pb_6, Using Different Methods[a]

| | Relative Energy (kJ mol^{-1}) | | | | | |
| | O_h | | D_{4h} | | C_{5v} | |
Method	1c	2c	1c	2c	1c	2c
RPA		0.0	0.0*	1.1	148.2*	132.7
HF	208.8	0.0	0.0	33.4	152.2	102.0
B3LYP	103.9	0.0	0.0	15.6	124.3	105.7
TPSS	82.3	0.0	0.0	1.0	148.1	127.7
PBE	79.0	0.0	0.0	3.9	135.0	116.0

[a]Asterisk (*) denotes that the O_h-symmetric isomer is not considered in the 1c energy comparison. All calculated values were obtained using dhf-QZVPP-2c basis sets and dhf-ecp-2c spin-orbit effective core potentials (ECPs).

A 2c MP2 study yielded a slight preference for the D_{4h}-symmetric structure.[39]

For all 1c methods, the D_{4h}-symmetric isomer (singlet occupation) is lowest in energy. At the 1c PBE, TPSS, and B3LYP levels, it is followed by the O_h-symmetric structure (triplet occupation), which is 79.0, 82.3, and 103.9 kJ mol^{-1} higher in energy, respectively. The PBE and B3LYP results are in good agreement with the values by Armbruster et al. that were previously mentioned.[38] The C_{5v}-symmetric structure (singlet occupation) is higher in energy than the O_h-symmetric structure by 20.4 kJ mol^{-1} (B3LYP) to 65.8 kJ mol^{-1} (TPSS). At the HF level, the energetic sequence is interchanged: C_{5v} is 152.2 kJ mol^{-1} and O_h 208.8 kJ mol^{-1} higher in energy than D_{4h}, indicating that the inclusion of HF exchange disfavors the O_h-symmetric structure significantly. No calculation was possible at the (correlated) 1c RPA level for the highly symmetric O_h isomer, since the t_{1u} representation (HOMO) is partly filled in the respective reference-state calculation.

The degeneracy of this partly occupied HOMO of the O_h-symmetric isomer is lifted by SOC. Therefore, at the 2c level, Jahn–Teller distortion does not occur. The D_{4h}-symmetric isomer (Kramers-restricted "singlet" occupation) and the O_h-symmetric one (Kramers-restricted "singlet" occupation) are almost isoenergetic with RPA (TPSS) preferring O_h symmetry by 1.1 kJ mol^{-1} (1.0 kJ mol^{-1}). In the case of PBE, B3LYP, and HF, O_h symmetry is preferred, by 3.9, 15.6, and 33.4 kJ mol^{-1}, respectively, which, again, is in good agreement with the values (PBE and B3LYP) obtained by Armbruster et al.[38] The C_{5v}-symmetric structure (Kramers-restricted "singlet" occupation) is significantly higher in energy than both the D_{4h}- and the O_h-symmetric structure by 68.6–132.7 kJ mol^{-1} for all 2c treatments.

Overall, it is found in this work, in agreement with earlier investigations,[38,76,77] that SOC removes the distinct energetical preference of the Jahn–Teller distorted D_{4h}-symmetric isomer of Pb_6. As a result, the D_{4h}-symmetric and the highly symmetric O_h structure can be regarded as isoenergetic, since the absolute values of the relative energies are very small for both RPA and TPSS. The latter is often considered to be most accurate within DFT when heavy-metal clusters are studied with an error in relative energies of <10 kJ mol^{-1}, compared to results obtained with the coupled-cluster singles and doubles with perturbative triples (CCSD(T)) approach.[78,79] Results obtained with RPA and TPSS are very similar, whereas, in particular, at the B3LYP and HF level, the energetical preference of D_{4h} symmetry is more prominent. Also of note is that the MP2 results[39] (slightly

preferring D_{4h} symmetry at the 2c level) are, to a certain extent, in agreement with the results presented in this work, despite comparably small HOMO–LUMO gaps at the HF level of ca. 5 eV for all studied isomers.

Finally, the computational effort is listed for the 1c and 2c RPA correlation energy computations on the D_{4h}-symmetric isomer of Pb_6. The energetically lowest 24 orbital/spinor pairs were excluded from the correlation treatment, thus correlating the remaining 84 electrons. Point group symmetry was not exploited and all calculations were carried out on a single Intel Xeon E5640 2.67 GHz processor, using 200 grid points in the Clenshaw–Curtis quadrature. The RI approximation was utilized and the dhf-QZVPP-2c basis set for Pb (714 basis functions in total) used. At the 1c RPA level using an unrestricted (Kohn–Sham) determinant as a reference, the computation time amounts to 70 min. At the respective 2c level, it is 278 min, which is an increase in computation time by a factor of 4, as expected.

5. CONCLUSIONS

The correlation energy within the 2c random phase approximation (RPA) formalism accounting for spin-orbit coupling (SOC) was derived, arriving at the plasmon equation, which is analogous to the one derived in 1c RPA formalism—namely, the sum over all time-dependent Hartree (TDH) excitation energies minus all TDH excitation energies within the Tamm–Dancoff approximation (TDA)—but with the respective excitation energies calculated within a 2c formalism. It was then shown that the sum over all 2c TDH excitation energies can exactly be rewritten as the trace over a Hermitian matrix for (Kramers-restricted) closed-shell systems using a very similar transformation as applied in 2c time-dependent density functional theory (TDDFT).[43,44] The resulting equation for the 2c RPA correlation energy was efficiently implemented in the TURBOMOLE program package in the same manner as in the 1c case,[14] representing the correlation energy as an integral over imaginary frequency using the RI approximation and an exponentially converging Clenshaw–Curtis quadrature. The ground-state equilibrium distances and harmonic vibrational frequencies of heavy diatomic molecules were calculated using the implemented 2c RPA method based on a 2c Kohn–Sham reference-state calculation utilizing 2c effective core potentials (ECPs) to account for SOC. Comparison to experiment shows that the errors with RPA are smaller than those obtained using Becke's three-parameter hybrid functional with Lee–Yang–Parr correlation (B3LYP), the functional of Perdew, Burke, and Ernzerhof (PBE), second-order Møller–Plesset perturbation theory (MP2), and Hartree–Fock theory (HF). The difference between the 1c and 2c level using RPA is in reasonable agreement with the differences obtained using the other methods. Finally, the efficiency was demonstrated by the calculation of the relative energies of the O_h-, D_{4h}-, and C_{5v}-symmetric isomers of Pb_6. It was found in agreement with earlier studies[38,76,77] that SOC removes the distinct energetical preference of the Jahn–Teller distorted D_{4h}-symmetric isomer and the D_{4h}-symmetric and the highly symmetric O_h structure can be regarded as isoenergetic.

■ APPENDIX: FOUR-COMPONENT RANDOM PHASE APPROXIMATION

In this Appendix, the plasmon equation (see eq 17) within a fully relativistic 4c theory, based on the Dirac–Coulomb–Breit Hamiltonian, is derived. The 4c Dirac–Coulomb–Breit

Hamiltonian (analogue of eq 1) is the expansion of the QED Hamiltonian up to $O(1/c^2)$ and reads, within the adiabatic connection formalism,[45,46,80−82]

$$\hat{\mathbf{H}}^\alpha = \hat{\mathbf{T}} + \hat{\mathbf{V}}^\alpha[j^\mu] + \alpha\hat{\mathbf{V}}_{ee}^{CB} \tag{37}$$

The kinetic energy operator of the electrons is given as

$$\hat{\mathbf{T}} = \sum_{\tilde{\sigma}} \sum_{i=1}^{N_{\tilde{\sigma}}} \hat{\mathbf{t}}_{i\tilde{\sigma}} \tag{38}$$

applying the so-called no-virtual-pair approximation, where the negative-energy continuum (or positronic) states are projected out and, therefore, the creation of virtual electron−positron pairs is not considered (which can be justified for low-energy processes). The one-electron Dirac kinetic energy operator (in atomic units, a.u.) is given as

$$\hat{\mathbf{t}}_{i\tilde{\sigma}} = c\vec{\boldsymbol{\alpha}}(i\tilde{\sigma})\cdot\hat{\vec{\pi}}_{i\tilde{\sigma}} + [\boldsymbol{\beta}(i\tilde{\sigma}) - \mathbf{1}]c^2 \tag{39}$$

$\hat{\vec{\pi}}_{i\tilde{\sigma}}$ is the kinetic momentum operator acting on electron $i\tilde{\sigma}$, and $\mathbf{1}$ is the 4×4 identity matrix. The three components of $\vec{\boldsymbol{\alpha}}$, as well as the $\boldsymbol{\beta}$ matrix, are given as

$$\boldsymbol{\alpha}_{x,y,z} = \begin{pmatrix} 0 & \boldsymbol{\sigma}_{x,y,z} \\ \boldsymbol{\sigma}_{x,y,z} & 0 \end{pmatrix} \qquad \boldsymbol{\beta} = \begin{pmatrix} \mathbf{1}_{2\times2} & 0 \\ 0 & -\mathbf{1}_{2\times2} \end{pmatrix} \tag{40}$$

with the 2×2 Pauli matrices being denoted as $\boldsymbol{\sigma}_{x,y,z}$.

α is the coupling strength parameter (which must not be confused with $\vec{\boldsymbol{\alpha}}$) that scales the interaction between the electrons (within the no-virtual-pair approximation)

$$\hat{\mathbf{V}}_{ee}^{CB} = \frac{1}{2}\sum_{\tilde{\sigma}\tilde{\sigma}'} \sum_{i=1}^{N_{\tilde{\sigma}}} \sum_{j=1}^{N_{\tilde{\sigma}'}} \hat{\mathbf{v}}_{i\tilde{\sigma}j\tilde{\sigma}'}^{CB} \qquad \text{for } i\tilde{\sigma} \neq j\tilde{\sigma}' \tag{41}$$

$\hat{\mathbf{v}}_{i\tilde{\sigma}j\tilde{\sigma}'}^{CB}$ is the two-electron Coulomb−Breit operator:

$$\hat{\mathbf{v}}_{i\tilde{\sigma}j\tilde{\sigma}'}^{CB} = \frac{1}{|\vec{r}_{i\tilde{\sigma}} - \vec{r}_{j\tilde{\sigma}'}|}\mathbf{1} - \frac{1}{2|\vec{r}_{i\tilde{\sigma}} - \vec{r}_{j\tilde{\sigma}'}|}$$
$$\times \left[\vec{\boldsymbol{\alpha}}(i\tilde{\sigma})\cdot\vec{\boldsymbol{\alpha}}(j\tilde{\sigma}') + \frac{[\vec{\boldsymbol{\alpha}}(i\tilde{\sigma})\cdot(\vec{r}_{i\tilde{\sigma}} - \vec{r}_{j\tilde{\sigma}'})][\vec{\boldsymbol{\alpha}}(j\tilde{\sigma}')\cdot(\vec{r}_{i\tilde{\sigma}} - \vec{r}_{j\tilde{\sigma}'})]}{|\vec{r}_{i\tilde{\sigma}} - \vec{r}_{j\tilde{\sigma}'}|^2}\right]$$
$$\text{for } i\tilde{\sigma} \neq j\tilde{\sigma}' \tag{42}$$

The first term in eq 42 describes the bare instantaneous Coulomb interaction, which is diagonal in 4c spin space. The second and third terms represent the Breit contribution; the second term (Gaunt term) arises due to magnetic interactions between the electrons, while the third term represents retardation effects.

$\hat{\mathbf{V}}^\alpha[j^\mu]$ constrains that the ground state $|\Psi_0^\alpha\rangle$ yields the interacting ground-state 4-current density $j^\mu = (c\rho, \vec{j})$ for all α.[47,80−82]

Analogously to eqs 2 and 3, the correlation energy $E_C^{CB}[\rho,\vec{j}]$ can be expressed by a coupling strength integral.[45,46] To evaluate the coupling strength integrand $W_C^{\alpha CB}[\rho,\vec{j}]$, the Coulomb−Breit interaction (eq 41) is expressed using the 4c electron field operators $\hat{\psi}^\dagger(\vec{r})$ as

$$\hat{\mathbf{V}}_{ee}^{CB} = \frac{1}{2}\int d^3r_1 \int d^3r_1 \left[\frac{\hat{\psi}^\dagger(\vec{r}_1)\hat{\psi}^\dagger(\vec{r}_2)\mathbf{1}\hat{\psi}(\vec{r}_1)\hat{\psi}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}\right.$$
$$- \frac{\hat{\psi}^\dagger(\vec{r}_1)\hat{\psi}^\dagger(\vec{r}_2)\vec{\boldsymbol{\alpha}}(1)\cdot\vec{\boldsymbol{\alpha}}(2)\hat{\psi}(\vec{r}_1)\hat{\psi}(\vec{r}_2)}{2|\vec{r}_1 - \vec{r}_2|}$$
$$\left.- \frac{\hat{\psi}^\dagger(\vec{r}_1)\hat{\psi}^\dagger(\vec{r}_2)[\vec{\boldsymbol{\alpha}}(1)\cdot(\vec{r}_1 - \vec{r}_2)][\vec{\boldsymbol{\alpha}}(2)\cdot(\vec{r}_1 - \vec{r}_2)]\hat{\psi}(\vec{r}_1)\hat{\psi}(\vec{r}_2)}{2|\vec{r}_1 - \vec{r}_2|^3}\right] \tag{43}$$

The fermion anticommutation relations are used to factorize the enumerators (the first one is the two-electron density operator and the second one is the two-electron current density operator, both with a prefactor of 2) into products of the one-electron density operator $\hat{\rho}(\vec{r})$ and the one-electron current density operator $\hat{\vec{j}}(\vec{r}) = c\hat{\psi}^\dagger(\vec{r})\vec{\boldsymbol{\alpha}}\hat{\psi}(\vec{r})$. With this definition of the one-electron current density operator, the 4-current density j^μ fulfills the continuity equation $\partial_\mu j^\mu = 0$. Analogously to eq 5, the density fluctuation operator $\Delta\hat{\rho}(\vec{r})$ and the current density fluctuation operator $\Delta\hat{\vec{j}}(\vec{r}) = \hat{\vec{j}}(\vec{r}) - \vec{j}(\vec{r})$ are introduced. All one-electron terms cancel, since the 4-current density j^μ is independent of α and the resulting expression for the Coulomb−Breit coupling strength integrand is

$$W_C^{\alpha CB} = \frac{1}{2}\int d^3r_1 \int d^3r_2$$
$$\times \left[\frac{\langle\Psi_0^\alpha|\Delta\hat{\rho}(\vec{r}_1)\mathbf{1}\Delta\hat{\rho}(\vec{r}_2)\mathbf{1}|\Psi_0^\alpha\rangle - \langle\Psi_0^0|\Delta\hat{\rho}(\vec{r}_1)\mathbf{1}\Delta\hat{\rho}(\vec{r}_2)\mathbf{1}|\Psi_0^0\rangle}{|\vec{r}_1 - \vec{r}_2|}\right.$$
$$- \frac{\langle\Psi_0^\alpha|\Delta\hat{\vec{j}}(\vec{r}_1)\mathbf{1}\cdot\Delta\hat{\vec{j}}(\vec{r}_2)\mathbf{1}|\Psi_0^\alpha\rangle - \langle\Psi_0^0|\Delta\hat{\vec{j}}(\vec{r}_1)\mathbf{1}\cdot\Delta\hat{\vec{j}}(\vec{r}_2)\mathbf{1}|\Psi_0^0\rangle}{2c^2|\vec{r}_1 - \vec{r}_2|}$$
$$\left.- \left(\frac{\langle\Psi_0^\alpha|[\Delta\hat{\vec{j}}(\vec{r}_1)\mathbf{1}\cdot(\vec{r}_1 - \vec{r}_2)][\Delta\hat{\vec{j}}(\vec{r}_2)\mathbf{1}\cdot(\vec{r}_1 - \vec{r}_2)]|\Psi_0^\alpha\rangle}{2c^2|\vec{r}_1 - \vec{r}_2|^3}\right)\right] \tag{44}$$

Defining the one-electron transition densities ρ_{0n}^α analogously to eq 6, along with the complex one-electron transition current densities,

$$\vec{j}_{0n}^\alpha(\vec{r}) = \langle\Psi_0^\alpha|\hat{\vec{j}}(\vec{r})\mathbf{1}|\Psi_n^\alpha\rangle \tag{45}$$

and inserting the completeness of the electronic states $|\Psi_0^\alpha\rangle$ ($n = 0, 1, 2, ...$) at any α, the exact correlation energy is given as in eq 7 but with the Hartree energy functional (eq 8), which only depends on ρ_{0n}, replaced by the real Coulomb−Breit energy functional

$$E_{CB}[\rho_{0n}^\alpha, \vec{j}_{0n}^\alpha] = \frac{1}{2}\int d^3r_1 \int d^3r_2 \left[\frac{\rho_{0n}^\alpha(\vec{r}_1)(\rho_{0n}^\alpha(\vec{r}_2))^*}{|\vec{r}_1 - \vec{r}_2|} - \frac{\vec{j}_{0n}^\alpha(\vec{r}_1)\cdot(\vec{j}_{0n}^\alpha(\vec{r}_2))^*}{2c^2|\vec{r}_1 - \vec{r}_2|}\right.$$
$$\left.- \frac{[\vec{j}_{0n}^\alpha(\vec{r}_1)\cdot(\vec{r}_1 - \vec{r}_2)][(\vec{j}_{0n}^\alpha(\vec{r}_2))^*\cdot(\vec{r}_1 - \vec{r}_2)]}{2c^2|\vec{r}_1 - \vec{r}_2|^3}\right] \tag{46}$$

depending on both ρ_{0n}^α and $\vec{j}_{0n}^\alpha$.

These transition densities and transition current densities can be calculated by solving the 4c TDKS eigenvalue problem[51−53,83−86] (4c analogues of eqs 9 and 10). Within 4c RPA (TDH or, strictly speaking, time-dependent Coulomb-Breit theory), the Hermitian orbital rotation Hessians are

$$A_{i\tilde{\sigma}a\tilde{\tau}j\tilde{\sigma}'b\tilde{\tau}'}^{\alpha RPA,CB} = (\varepsilon_{a\tilde{\tau}} - \varepsilon_{i\tilde{\sigma}})\delta_{ij}\delta_{ab}\delta_{\tilde{\sigma}\tilde{\sigma}'}\delta_{\tilde{\tau}\tilde{\tau}'} + \alpha\langle\Phi_{i\tilde{\sigma}}\Phi_{b\tilde{\tau}'}|\hat{\mathbf{v}}_{12}^{CB}|\Phi_{a\tilde{\tau}}\Phi_{j\tilde{\sigma}'}\rangle \tag{47}$$

$$B_{i\tilde{\sigma}a\tilde{\tau}j\tilde{\sigma}'b\tilde{\tau}'}^{\alpha RPA,CB} = \alpha\langle\Phi_{i\tilde{\sigma}}\Phi_{j\tilde{\sigma}'}|\hat{\mathbf{v}}_{12}^{CB}|\Phi_{a\tilde{\tau}}\Phi_{b\tilde{\tau}'}\rangle \tag{48}$$

In contrast to eqs 11 and 12, the orbital rotation Hessians contain additional (two-electron) terms arising from the Breit interaction. $\varepsilon_{p\tilde{\sigma}}$ is the energy of 4c spinor $\Phi_{p\tilde{\sigma}}$. The first-order RPA/TDH transition density is given analogously to eq 13, while the complex first-order RPA/TDH transition current density is introduced as

$$\vec{j}_{0n}^{\alpha RPA,CB(1)}(\omega_n^\alpha, \vec{r})$$

$$= \sum_{\tilde\sigma\tilde\tau} \sum_{i=1}^{N_{\tilde\sigma}} \sum_{a=N_{\tilde\tau}+1}^{M_{\tilde\tau}} cX_{i\tilde\sigma a\tilde\tau,n}^{\alpha RPA,CB}(\omega_n^\alpha)\Phi_{i\tilde\sigma}^\dagger(\vec{r})\vec{\alpha}\Phi_{a\tilde\tau}(\vec{r})$$

$$+ cY_{i\tilde\sigma a\tilde\tau,n}^{\alpha RPA,CB}(\omega_n^\alpha)\Phi_{a\tilde\tau}^\dagger(\vec{r})\vec{\alpha}\Phi_{i\tilde\sigma}(\vec{r}) \qquad (49)$$

With eqs 7 and 46, the correlation energy is then given analogously to eq 14 but with $1/|\vec{r}_1 - \vec{r}_2|$ replaced by $\hat{\mathbf{v}}_{12}^{CB}$. Applying the Hellmann–Feynman theorem[50] to the 4c analogue of eq 9 and comparing to the 4c analogue of eq 7, it follows (analogous to eq 15) that

$$\frac{d\omega_n^{\alpha RPA,CB}}{d\alpha} = 2E_{CB}[\rho_{0n}^{\alpha RPA,CB(1)}, \vec{j}_{0n}^{\alpha RPA,CB(1)}] \qquad (50)$$

Carrying out the coupling strength integration analytically, one finally arrives at the plasmon formula:

$$E_C^{RPA,CB} = \frac{1}{2}\sum_n (\omega_n^{RPA,CB} - \omega_n^{TDA\,RPA,CB}) \qquad (51)$$

which is analogous to eq 17 but with the respective excitation energies calculated using modified orbital rotation Hessians (see eqs 47 and 48, where $1/|\vec{r}_1 - \vec{r}_2|$ is replaced by $\hat{\mathbf{v}}_{12}^{CB}$). Also, reference-state spinors and their energies are obtained within ground-state KS theory based on the Dirac–Coulomb–Breit Hamiltonian (eq 37).

The 4c Dirac–Coulomb Hamiltonian is obtained by neglecting the Breit contribution (the second and third terms in eq 42), which leads to a plasmon formula analogous to eq 51 (or eq 17). Within 4c Dirac–Coulomb–Breit RPA, two-electron magnetic and retardation effects on the ground-state correlation energy are considered, whereas within 4c Dirac–Coulomb RPA, such effects are not taken into account and electrons are considered to interact instantaneously via the bare (electrical) Coulomb interaction. As a result, transition current densities (eq 45) do not appear in the derivation of the plasmon formula. To arrive at the 2c formalism presented in section 2.1, the electronic components of the 4c Dirac–Coulomb Hamiltonian are decoupled from the positronic ones and only the former are considered. This decoupling can be done by the (all-electron) X2C approach,[37] where the one-electron part of the 4c Hamiltonian is decoupled exactly (however, the so-called "picture change error" is introduced), or simply by adding 2c one-electron contributions to the 1c Hamiltonian arising from 2c (valence-only) ECPs that are fitted to 4c multiconfiguration Dirac–Hartree–Fock calculations on atoms.[30−36] The structure of the equations needed to derive the plasmon formula is the same in the 2c case and within 4c Dirac–Coulomb theory (see section 2.1), since all two-electron operators are the same and one does not have to take transition current densities into account.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table with equilibrium distances and vibrational frequencies of At_2 calculated using different 2c and 1c methods. Coordinates of all isomers of Pb_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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