

RESEARCH ARTICLE | SEPTEMBER 22 2026

^{13}C and ^{19}F nucleus–electron correlation and self-energies

Janina Vohdin ; Christof Holzer  



J. Chem. Phys. 165, 124109 (2026)

<https://doi.org/10.1063/5.0341164>



Articles You May Be Interested In

Approaching the basis-set limit of the dRPA correlation energy with explicitly correlated and projector augmented-wave methods

J. Chem. Phys. (November 2022)

Self-consistent Kohn-Sham method based on the adiabatic-connection fluctuation-dissipation theorem and the exact-exchange kernel

J. Chem. Phys. (June 2015)

Robust and accurate hybrid random-phase-approximation methods

J. Chem. Phys. (October 2019)



The Journal of Chemical Physics

Special Topics Open for Submissions

[Learn More](#)

^{13}C and ^{19}F nucleus–electron correlation and self-energies

Cite as: J. Chem. Phys. 165, 124109 (2026); doi: 10.1063/5.0341164

Submitted: 29 April 2026 • Accepted: 28 August 2026 •

Published Online: 22 September 2026



Janina Vohdin  and Christof Holzer^{a)} 

AFFILIATIONS

Institute of Quantum Materials and Technologies, Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

^{a)} Author to whom correspondence should be addressed: holzer@kit.edu

ABSTRACT

We present a theoretical and numerical study of the correlation between electrons and the fermionic ^{13}C and ^{19}F nuclei. We use the random-phase approximation (RPA) as a valuable tool in obtaining these correlation energies. A special connection between the RPA and second-order perturbation theory for the inter-fermionic interaction is outlined. Subsequently, Green's function-based GW self-energies are evaluated for the nuclear densities. The strong influence of self-interaction errors is demonstrated, and vertex corrections are shown to be strictly necessary to obtain reasonable results. The theoretical and technical requirements for a quantum mechanical treatment of ^{13}C and ^{19}F nuclei are also addressed in this study, thereby facilitating further research in this area.

© 2026 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0341164>

I. INTRODUCTION

Since the introduction of the Born–Oppenheimer (BO) approximation, molecular quantum mechanics has strongly relied on it.¹ Born and Oppenheimer rigorously demonstrated this to be an excellent approximation under most circumstances. Countless investigations and real-world applications have confirmed the accuracy of the BO approximation; therefore, there is no need to abandon it for the majority of quantum chemical applications. Our curiosity nevertheless leads to many questions, such as how the quantum chemical world functions beyond the BO approximation.^{2–4} For example, understanding the behavior of two fermions in the high-density limit is crucial for understanding the correct asymptotic behavior of correlation energy functionals.⁵ Although so far two-electron systems consisting of one spin-up and one spin-down electron have been used to parameterize the high-density limit of correlation,^{5–9} additional information on the behavior of the correlation between two different fermions is valuable. Investigations of the electron–proton correlation^{10–18} are more widely available, though no equivalent investigations exist for heavier fermions. In this study, we will therefore discuss important points about the interactions of fermionic ^{13}C and ^{19}F nuclei with their surrounding electrons. We therefore seek to present an initial implementation of

a general density functional theory framework applicable to heavier fermionic nuclei. We then focus on the principal correlation between electrons and the ^{13}C and ^{19}F nuclei, as well as the binding energies of the nuclei to the molecular systems. Despite the explicit nucleus–electron correlation being considered to be insignificant for standard quantum chemical applications, recent applications of generalized fermion density functional theory have highlighted the importance of understanding these kinds of interactions for the design of density functional approximations.⁵ Our interest in the details of electron–nucleus correlation has been further stimulated by recent observations of quantum tunneling involving heavier nuclei.^{19–22} For the latter, explicit simulations of quantum nuclei embedded in electronic simulations will be of importance but still require solving a multitude of theoretical and technical issues. While the latter remains a goal for future study, this study aims to establish a solid and systematically improvable foundation toward its realization, providing the theoretical framework and methodological groundwork necessary for subsequent developments.

II. THEORY

Multicomponent DFT has been described in detail in the literature,^{23–28} and an application of the method to ^{13}C and ^{19}F

nuclei is straightforward, simply requiring one to modify the corresponding kinetic and potential energy terms according to the mass and charge of the particle used. This is also true for Coulomb integrals, which need to be adapted to charges larger than ± 1 , which we consider to be trivial. In this study, we use Gaussian basis functions, indicated by the Greek letter χ . The Latin letter ϕ denotes spin-dependent one-particle Kohn–Sham (KS) states. Therefore, the KS states of two fermions in the Gaussian basis set approximation read

$$q' = \phi'_q(x) = \left[\sum_{\mu} c'_{\mu,q} \chi'_{\mu}(r) \right], \quad (1)$$

$$q'' = \phi''_q(x) = \left[\sum_{\mu} c''_{\mu,q} \chi''_{\mu}(r) \right]. \quad (2)$$

As usual, σ denotes the spin of the fermion, $x = \{r, \sigma\}$ is a combined spatial-spin coordinate, and c denotes the KS coefficients. Unprimed indices q will be used to denote combined spaces of both fermions

$$q = \{q', q''\} = \{\phi'_q(x), \phi''_q(x)\}, \quad (3)$$

while separate spaces will be primed, as indicated by q' and q'' . Throughout this study, single-primed quantities refer to electrons, while double-primed quantities refer to nuclear fermions. The sets of one-electron functions q' and one-fermion functions q'' are obtained from multicomponent KS–DFT as outlined in the literature.^{29–31}

A. Correlation energies between fermions

To access the correlation energy between two different fermions, for example, electrons and ^{13}C or ^{19}F nuclei, we use the random-phase approximation (RPA) as a valuable tool. As shown in a recent review,³² the adiabatic connection (AC) is a key tool in obtaining correlation energies. Within the AC, a single coupling strength parameter, denoted α , is used to switch continuously from the non-interacting KS system to the many-fermion system. In the multicomponent framework, the coupling-strength-dependent AC Hamiltonian reads

$$\hat{H}_{\alpha}(\rho_e, \rho_f) = \hat{T}_e + \hat{T}_f + \hat{V}_{ne} + \hat{V}_{nf} + \hat{V}_{\alpha}(\rho_e, \rho_f) + \alpha(\hat{V}_{ee} + \hat{V}_{ef} + \hat{V}_{ff}), \quad (4)$$

where $\hat{T}$ denotes the kinetic-energy operators of electrons and nuclei, respectively, $\hat{V}_{ne}$ and $\hat{V}_{nf}$ are the nucleus–electron and nucleus–fermion Coulomb operators, $\hat{V}_{\alpha}(\rho_e, \rho_f)$ is a one-fermion local operator determined by the density constraint, and $\alpha(\hat{V}_{ee} + \hat{V}_{ef} + \hat{V}_{ff})$ collects all fermion–fermion Coulomb interactions. Quantities with the subscript e denote electrons, whereas those with the subscript f denote nuclear fermions. It is noted that $\hat{V}_{ff}$ vanishes for the systems considered here because only one particle of the nuclear–fermion species is treated as a quantum object. Similar to standard Born–Oppenheimer KS and AC theory, $\hat{V}_{\alpha}(\rho_e, \rho_f)$ turns into the Hartree, exchange, and correlation potential in the non-interacting limit.³² This essentially yields the KS determinant

as the ground-state wave function, and the missing correlation is to be determined as

$$E = \langle \phi | \hat{H}_{\alpha=1} | \phi \rangle + E^C, \quad (5)$$

where $\hat{H}_{\alpha=1}$ is the fully interacting multicomponent Hamiltonian defined in the preceding equation and ϕ is the reference determinant. Therefore, $\langle \phi | \hat{H}_{\alpha=1} | \phi \rangle$ is the correlation-free reference energy; it is not the expectation value of a Fock operator.³³ Following standard procedures, we obtain

$$E^C(\rho_e, \rho_f) = \int_0^1 d\alpha \left(\langle \psi_{\alpha}(\rho_e, \rho_f) | \hat{V}_{ee} + \hat{V}_{ef} + \hat{V}_{ff} | \psi_{\alpha}(\rho_e, \rho_f) \rangle - \langle \phi(\rho_e, \rho_f) | \hat{V}_{ee} + \hat{V}_{ef} + \hat{V}_{ff} | \phi(\rho_e, \rho_f) \rangle \right), \quad (6)$$

where ψ_{α} is the interacting ground-state wave function with scaled electron–electron, electron–fermion, and fermion–fermion interactions. Using the fluctuation–dissipation theorem, we can re-express the correlation energy as an imaginary integral, yielding³⁴

$$E^C(\rho_e, \rho_f) = \frac{1}{4\pi} \int_0^1 d\alpha \operatorname{Im} \int_{-\infty}^{\infty} d\omega \frac{\kappa_{\alpha}(x_1, x_2, \omega) - \kappa_0(x_1, x_2, \omega)}{|\mathbf{r} - \mathbf{r}'|}, \quad (7)$$

with $\kappa_{\alpha}(x_1, x_2, \omega)$ being the frequency-dependent linear response function. Next, we define the multicomponent time-dependent density-matrix–density-matrix response function

$$\Pi_{\alpha}(\omega) = \left[\begin{pmatrix} \mathbf{A}' & \mathbf{B}' & \mathbf{C}^T & \mathbf{C}^T \\ \mathbf{B}' & \mathbf{A}' & \mathbf{C}^T & \mathbf{C}^T \\ \mathbf{C} & \mathbf{C} & \mathbf{A}'' & \mathbf{B}'' \\ \mathbf{C} & \mathbf{C} & \mathbf{B}'' & \mathbf{A}'' \end{pmatrix} - (\omega + i\eta) \begin{pmatrix} \mathbf{1} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & -\mathbf{1} \end{pmatrix} \right]^{-1}, \quad (8)$$

with the matrix elements

$$A'_{i'a', j'b'} = (\epsilon_{i'a'} - \epsilon_{j'b'}) \delta_{i'j'} \delta_{a'b'} + \alpha(i'a' | b'j') + f_{i'a', j'b'}^{\text{XC}, \alpha}(\omega), \quad (9)$$

$$A''_{i''a'', j''b''} = (\epsilon_{i''a''} - \epsilon_{j''b''}) \delta_{i''j''} \delta_{a''b''} + \alpha(i''a'' | b''j'') + f_{i''a'', j''b''}^{\text{XC}, \alpha}(\omega), \quad (10)$$

$$B'_{i'a', j'b'} = (i'a' | j'b') + f_{i'a', j'b'}^{\text{XC}, \alpha}(\omega), \quad (11)$$

$$B''_{i''a'', j''b''} = (i''a'' | j''b'') + f_{i''a'', j''b''}^{\text{XC}, \alpha}(\omega), \quad (12)$$

$$C_{i'a', j''b''} = (i'a' | j''b''). \quad (13)$$

$\kappa_{\alpha}(x_1, x_2, \omega)$ can then be obtained from Eq. (8) as

$$\kappa_{\alpha}(\omega, x_1, x_2) = \Pi_{\alpha}(\omega, x_1, x_1, x_2, x_2), \quad (14)$$

connecting both quantities. While this relation is convenient to demonstrate the connection, we prefer to re-express Eq. (7) using the Bethe–Salpeter equation, re-formulating Eq. (8) as

$$\Pi_{\alpha}(\omega) = \Pi_0(\omega) + \Pi_0(\omega) (\alpha \mathbf{V} + \mathbf{F}_{\alpha}^{\text{XC}}(\omega)) \Pi_{\alpha}(\omega). \quad (15)$$

In Eq. (15), $\Pi_0(\omega) = \Pi_{\alpha=0}(\omega)$, and $\mathbf{V}$ collects all Coulomb contributions from Eqs. (9)–(13), while $\mathbf{F}_\alpha^{\text{XC}}(\omega)$ collects the remaining exchange-correlation contributions from these equations. This finally leads to the correlation energy being obtained as^{17,35–37}

$$E^{\text{C}} = \frac{1}{4\pi} \int_0^1 d\alpha \operatorname{Im} \int_{-\infty}^{\infty} d\omega \operatorname{Tr} [\mathbf{V}(\Pi_\alpha(\omega) - \Pi_0(\omega))], \quad (16)$$

using a double integral over imaginary frequencies and the coupling strength α . As we do not know the exact nature of f_α^{XC} , we introduce two approximations to make Eq. (16) integrable. First, we consider the adiabatic approximation, making it independent of the frequency ω . Second, we assume that it is only a weak function of the coupling strength α , so we can also neglect this dependence. The exchange-correlation part can therefore be expressed as

$$f_{ia,jb}^{\text{XC},\alpha}(\omega) \approx \alpha \frac{\partial^2 E}{\partial \rho_{ia} \partial \rho_{jb}}. \quad (17)$$

This allows us to rewrite Eq. (15) as

$$\Pi_\alpha(\omega) = \Pi_0(\omega) + \alpha \Pi_0(\omega) (\mathbf{V} + \mathbf{F}^{\text{XC}}) \Pi_\alpha(\omega). \quad (18)$$

Using Eq. (18), both integrations in Eq. (16) can be performed analytically, leading to

$$E^{\text{C}} = \frac{1}{2} \left(\sum_n \Omega_n^+ - \operatorname{Tr}(\mathbf{A}') - \operatorname{Tr}(\mathbf{A}'') \right), \quad (19)$$

where Ω_n^+ denotes the poles on the excitation branch of the interacting response function. The superscript + refers to the positive symplectic norm of the corresponding response vector, not necessarily to the sign of the eigenvalue. For the multicomponent vectors used here, this norm is

$$\mathcal{N}_n = X_n'^\dagger X_n' + X_n''^\dagger X_n'' - Y_n'^\dagger Y_n' - Y_n''^\dagger Y_n''.$$

Excitations have $\mathcal{N}_n > 0$, whereas their time-reversed de-excitation partners have $\mathcal{N}_n < 0$. The eigenvalues Ω can be extracted from the eigenvalue problem

$$\begin{pmatrix} \mathbf{A}' & \mathbf{B}' & \mathbf{C}^T & \mathbf{C}^T \\ -\mathbf{B}' & -\mathbf{A}' & -\mathbf{C}^T & -\mathbf{C}^T \\ \mathbf{C} & \mathbf{C} & \mathbf{A}'' & \mathbf{B}'' \\ -\mathbf{C} & -\mathbf{C} & -\mathbf{B}'' & -\mathbf{A}'' \end{pmatrix} \begin{pmatrix} X' \\ Y' \\ X'' \\ Y'' \end{pmatrix} = \Omega \begin{pmatrix} X' \\ Y' \\ X'' \\ Y'' \end{pmatrix}. \quad (20)$$

If the orbital Hessian in Eq. (8) is positive semidefinite, the positive-norm excitation branch coincides with the positive eigenvalues. For a non-positive-definite Hessian, however, the sign of the eigenvalue can be misleading, and $\mathcal{N}_n$ must be evaluated explicitly to distinguish excitations from de-excitations.

Equation (19) yields the total correlation energy of the system. To extract electron–fermion correlation energies, we evaluate Eq. (19) also with the modified uncoupled matrix

$$\begin{pmatrix} \mathbf{A}' & \mathbf{B}' & \mathbf{0} & \mathbf{0} \\ -\mathbf{B}' & -\mathbf{A}' & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{A}'' & \mathbf{B}'' \\ \mathbf{0} & \mathbf{0} & -\mathbf{B}'' & -\mathbf{A}'' \end{pmatrix} \begin{pmatrix} X' \\ Y' \\ X'' \\ Y'' \end{pmatrix} = \Omega^{\text{unc.}} \begin{pmatrix} X' \\ Y' \\ X'' \\ Y'' \end{pmatrix}, \quad (21)$$

and obtain the electron–¹³C and electron–¹⁹F correlation energies as

$$E_{e-f}^{\text{C}} = E^{\text{C}} - E_{\text{unc.}}^{\text{C}}, \quad (22)$$

$$E_{e-f}^{\text{C}} = \frac{1}{2} \sum_n (\Omega_n^+ - \Omega_{n,\text{unc.}}^+). \quad (23)$$

The correlation energy between different fermions can therefore be described as half the difference between the excitation energies of the fully coupled and uncoupled systems. We have not yet introduced approximations beyond the independence from frequency and coupling strength of the terms involved in the calculation of $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$. The simplest approximation, neglecting f^{XC} entirely, is called direct RPA (dRPA). While being the most commonly used RPA variant in electronic structure theory, it suffers from self-interaction errors (SIE). Especially for nuclear wave functions originating from highly charged fermions, the SIE can become extensive. Including f^{XC} will be referred to as a “vertex” correction³⁸ and ideally removes the SIE. We will therefore test the impact of different approximations in the blue and red blocks shown in Eqs. (20) and (21).

B. Connection to second-order perturbation theory

The connection of the diagonal RPA approximation to MP2 becomes apparent in the direct ring coupled-cluster doubles (drCCD) formulation of RPA.³⁹ With $\mathbf{T} = \mathbf{Y}\mathbf{X}^{-1}$, the RPA eigenvalue problem is equivalent to the drCCD Riccati equation and energy expression

$$\mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T} = 0, \quad (24)$$

$$E^{\text{C,RPA}} = \frac{1}{2} \operatorname{Tr}(\mathbf{B}\mathbf{T}). \quad (25)$$

We now consider the diagonal approximation, $\mathbf{A}' = \mathbf{D}'$, $\mathbf{A}'' = \mathbf{D}''$, and $\mathbf{B}' = \mathbf{B}'' = 0$, such that the interaction-dependent parts contain only the off-diagonal inter-fermion blocks. To obtain its perturbative limit, we introduce a coupling parameter λ and the expansions

$$\mathbf{A}(\lambda) = \mathbf{D} + \lambda \mathbf{A}^{(1)}, \quad (26)$$

$$\mathbf{B}(\lambda) = \lambda \mathbf{B}^{(1)}, \quad (27)$$

$$\mathbf{T}(\lambda) = \lambda \mathbf{T}^{(1)} + \mathcal{O}(\lambda^2), \quad (28)$$

where $D_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab}$. Insertion into the Riccati residual $\mathcal{R} = \mathbf{B} + \mathbf{A}\mathbf{T} + \mathbf{T}\mathbf{A} + \mathbf{T}\mathbf{B}\mathbf{T}$ yields at first order

$$\mathcal{R}^{(1)} = \mathbf{B}^{(1)} + \mathbf{D}\mathbf{T}^{(1)} + \mathbf{T}^{(1)}\mathbf{D} = 0. \quad (29)$$

The mixed block of this residual, therefore, yields

$$T_{i'a',j''b''}^{(1)} = -\frac{(i'a'|j''b'')}{\varepsilon_{a'} + \varepsilon_{b''} - \varepsilon_{i'} - \varepsilon_{j''}}. \quad (30)$$

Inserting these amplitudes into the drCCD energy gives the inter-fermion MP2 correlation energy,

$$E_{e-f}^{\text{C,MP2}} = - \sum_{i' a' j'' b''} \frac{|(i' a' | j'' b'')|^2}{\varepsilon_{a'} + \varepsilon_{b''} - \varepsilon_{i'} - \varepsilon_{j''}}. \quad (31)$$

The factor 1/2 in the trace is canceled by the two off-diagonal electron–fermion blocks. The second-order coefficient of diagonal RPA is therefore given by Eq. (31), whereas the full RPA energy also contains higher-order rings. Formally,

$$E_{e-f}^{\text{C,diag}}(\lambda) = \lambda^2 E_{e-f}^{\text{C,MP2}} + \mathcal{O}(\lambda^4). \quad (32)$$

For completeness, Eq. (31) can be evaluated using a Laplace transformation.^{40–42} With the RI approximation $(i' a' | j'' b'') = \sum_P B_{i' a'}^P B_{j'' b''}^P$ and the intermediates

$$R_{PQ}'(t) = \sum_{i' a'} B_{i' a'}^P B_{i' a'}^Q e^{-t(\varepsilon_{a'} - \varepsilon_{i'})}, \quad (33)$$

$$S_{PQ}''(t) = \sum_{j'' b''} B_{j'' b''}^P B_{j'' b''}^Q e^{-t(\varepsilon_{b''} - \varepsilon_{j''})}, \quad (34)$$

the MP2 energy becomes

$$E_{e-f}^{\text{C,MP2}} = - \int_0^\infty dt \sum_{PQ} R_{PQ}'(t) S_{PQ}''(t). \quad (35)$$

This representation permits an $\mathcal{O}(N^4)$ evaluation of the electron–fermion MP2 correlation energy. If $\tilde{R}_{PQ}'(|t|)$ and $\tilde{S}_{PQ}''(|t|)$ denote the Fourier transforms of the even extensions $R_{PQ}'(|t|)$ and $S_{PQ}''(|t|)$, respectively, Parseval's theorem gives

$$E_{e-f}^{\text{C,MP2}} = - \frac{1}{2\pi} \int_0^\infty d\omega \sum_{PQ} \tilde{R}_{PQ}'(\omega) \tilde{S}_{PQ}''(\omega), \quad (36)$$

highlighting the relation to the RPA energy expression.

C. GW correlation self-energies in the random-phase approximation

The correlation part of the GW self-energy can be obtained as shown in Ref. 17 using contour deformation as

$$\Sigma_q^{\text{C}}(\omega^{\text{F}}) = \mathcal{R}_q^{\text{C}}(\omega^{\text{F}}) + \mathcal{I}_q^{\text{C}}(\omega^{\text{F}}). \quad (37)$$

The terms $\mathcal{R}_q^{\text{C}}(\omega^{\text{F}})$ and $\mathcal{I}_q^{\text{C}}(\omega^{\text{F}})$ are shown below. The imaginary-axis contribution $\mathcal{I}$ is

$$\mathcal{I}_q^{\text{C}}(\omega^{\text{F}}) = - \frac{1}{4\pi} \sum_{p'} \int_{-\infty}^\infty d\omega' \frac{W_{p'q'p'q'}^{\text{C}}(i\omega')}{\omega^{\text{F}} - \varepsilon_{p'}^{\text{F}} + \omega'}, \quad (38)$$

whereas the contribution $\mathcal{R}$ arising from Cauchy's residue theorem is

$$\mathcal{R}_q^{\text{C}}(\omega^{\text{F}}) = \sum_{p'} \mathcal{F}_{p'} \{ W_{p'q'p'q'}^{\text{C}}(\omega^{\text{F}} - \varepsilon_{p'}^{\text{F}}) \}. \quad (39)$$

$\mathcal{F}_{p'}$ is the contribution of the residue, equal to either ± 1 , ± 0.5 , or 0.⁴³ ω^{F} is the frequency with respect to the Fermi level, and we note

that the Fermi level must be chosen separately for each fermion. The screened exchange $\mathbf{W}^{\text{C}}$ is subsequently constructed from the solution vectors $\{X', Y', X'', Y''\}$ of the response matrix shown in Eq. (20) as described in Ref. 44. Different levels of vertex corrections can be built into $\mathbf{A}'$, $\mathbf{B}'$ and $\mathbf{A}''$, $\mathbf{B}''$ in a straightforward manner by simply modifying the matrix elements. Quasiparticle energies are subsequently obtained separately for each fermion from the underlying Kohn–Sham eigenvalues and the diagonal part of the self-energy as

$$\varepsilon_{q'}^{\text{QP}}(\omega) = \varepsilon_{q'}^{\text{KS}} + Z_{q'} \langle q' | \Sigma_{q'}^{\text{X}} + \Sigma_{q'}^{\text{C}}(\omega) - V_{q'}^{\text{KS}} | q' \rangle, \quad (40)$$

$$\varepsilon_{q''}^{\text{QP}}(\omega) = \varepsilon_{q''}^{\text{KS}} + Z_{q''} \langle q'' | \Sigma_{q''}^{\text{X}} + \Sigma_{q''}^{\text{C}}(\omega) - V_{q''}^{\text{KS}} | q'' \rangle. \quad (41)$$

The quasiparticle energy of the nucleus thus corresponds to the energy required to remove it from the quantum mechanical system. For the carbon and fluorine nuclei investigated in this study, this causes the final state to be highly charged.

III. COMPUTATIONAL DETAILS

We consider the systems ^{13}C , $^{13}\text{CH}_4$, $^{13}\text{CClH}_3$, $^{13}\text{CCl}_3\text{H}$, $^{13}\text{CCl}_4$, $^{13}\text{CCl}_3\text{F}$, and $^{13}\text{CH}_2\text{ClF}$ for carbon and ^{19}F , $^{19}\text{F}^-$, $^{19}\text{F}_2$, H^{19}F , $\text{CCl}_3^{19}\text{F}$, $\text{CH}_2\text{Cl}^{19}\text{F}$, Au^{19}F , and Tl^{19}F for fluorine. These molecular systems were chosen to represent different bonding situations around the considered quantum nuclei. Therefore, both isolated atoms and various diatomic molecules were included for fluorine. Furthermore, hydrogen atoms bonded to the carbon quantum nucleus were successively replaced by halogen atoms. Initially, the geometries were optimized with standard Born–Oppenheimer DFT using the CHYF functional.⁵ In the following step, multicomponent KS solutions³⁰ were obtained by treating both the carbon and fluorine nuclei as quantum mechanical objects. The CHYF functional was used again due to its general fermion design.⁵ From the set of converged electronic and carbon/fluorine KS eigenstates, the RPA correlation energies, GW self-energies, and quasiparticle energies were subsequently calculated. Correlation energies from second-order Møller–Plesset (MP2) perturbation theory were obtained at the multicomponent HF reference states. Furthermore, MP2 calculations at the CHYF reference were used to validate the numerical near-equivalence to diagonal RPA outlined in Sec. II B. All investigations were performed using the decontracted aug-cc-pV6Z basis set for carbon and fluorine and the def2-QZVP basis set for the remaining elements if applicable. For Au and Tl, the x2c-TZVPPall-2c basis set was used.⁴⁵ When X2C was used,^{17,46} a finite nucleus model located at the center of mass of the nuclear density was employed.^{47,48} Basis sets for the quantum nuclei were optimized for the respective atoms and the CCl_3F molecule. The latter was chosen because of its relevance as a standard in nuclear magnetic resonance experiments and its low symmetry. For this purpose, a local development version of Turbomole^{49,50} was extended to include analytical gradients for arbitrarily charged fermions, enabling the construction of near-optimal basis sets even in these initial investigations. The resulting segmented contracted hexuple- ζ [11s8p4d3f2g1h] $\rightarrow$ [6s5p4d3f2g1h] nuclear basis sets are reported in the [supplementary material](#). Auxiliary basis sets were generated using the automatic procedure^{51,52} of ERKALE⁵³ from a union of the electronic and

nuclear basis sets. To consistently cover all fitting cases in the auxiliary basis set, the electronic decontracted aug-cc-pV6Z basis set was combined with the respective nucdef-6Z basis set. A threshold of 10^{-8} was chosen in the Cholesky decomposition while generating the auxiliary basis set, yielding functions with angular momentum up to $l = 10$.⁵² The auxiliary basis sets are reported in the [supplementary material](#).

A. RPA approximations

As introduced in Sec. II A, the adiabatic (frequency-independent) and coupling-strength-independent exchange-correlation kernel $\mathbf{F}^{\text{XC}}$ entering Eq. (18) is the working approximation to the exact, but unknown, time-dependent exchange-correlation kernel $f_{\alpha}^{\text{XC}}(\omega)$. We refer to $\mathbf{F}^{\text{XC}}$ as the “adiabatic vertex” throughout this study and denote it as Γ

$$\Gamma \equiv \mathbf{F}^{\text{XC}}, \quad (42)$$

so that

$$\Gamma_{pq,rs} = \frac{\partial^2 E}{\partial D_{pq} \partial D_{rs}}. \quad (43)$$

We explicitly evaluate the matrix elements defined in Eq. (43) using the CHYF functional, which is equivalent to assembling the full adiabatic TD-DFT response matrix in the molecular-orbital basis. For any given block of the response matrix in Eqs. (20) and (21) (electron–electron, nucleus–nucleus, or electron–nucleus), we distinguish three approximations to the corresponding A and B matrix elements defined in Eqs. (9)–(13). First, neglecting Γ entirely, i.e., retaining only the bare Coulomb interaction, defines direct RPA (dRPA),

$$A_{ia,jb}^{\text{dRPA}} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (ia|bj), \quad (44)$$

$$B_{ia,jb}^{\text{dRPA}} = (ia|jb). \quad (45)$$

Second, including the adiabatic vertex in addition to the Coulomb interaction defines the vertex-corrected kernel, denoted by “+ Γ ,”

$$A_{ia,jb}^{+\Gamma} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + (ia|bj) + \Gamma_{ia,bj}, \quad (46)$$

$$B_{ia,jb}^{+\Gamma} = (ia|jb) + \Gamma_{ia,jb}, \quad (47)$$

consistent with the electron (') and nucleus (") matrix elements of Eqs. (9)–(13). Third, as already used in Sec. II B to establish the connection to MP2 theory, a diagonal approximation (“diag”) neglects Γ and, in addition, restricts A to its diagonal while setting B to zero,

$$A_{ia,jb}^{\text{diag}} = (\epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab}, \quad (48)$$

$$B^{\text{diag}} = \mathbf{0}. \quad (49)$$

Combining these approximations for the electron and nucleus blocks of Eqs. (20) and (21) yields the three RPA variants used in this study and summarized in Table I: (i) dRPA, using Eq. (44)

TABLE I. Definition of RPA variants used in this study. The name of the RPA variant is given. Reference denotes the reference state/calculation used, and electron (blue), nucleus (red), and elec.–nuc. (green) describe the corresponding approximations used to evaluate Eqs. (20) and (21).

name	Reference	Electron	Nucleus	Elec.–nuc.
dRPA	CHYF	dRPA	dRPA	RPA
dRPA+ Γ	CHYF	dRPA	$V + \mathbf{F}^{\text{XC}}$	RPA
diag+ Γ	CHYF	diag	$V + \mathbf{F}^{\text{XC}}$	RPA
MP2	HF	...	...	MP2

for both the electron and nucleus blocks; (ii) dRPA+ Γ , retaining Eq. (44) for the electron block but using the vertex-corrected kernel of Eq. (46) for the nucleus block; and (iii) diag+ Γ , using the diagonal approximation of Eq. (48) for the electron block together with the vertex-corrected nucleus block of Eq. (46). In all three variants, the electron–nucleus block C retains only the bare Coulomb interaction [Eq. (13)], which we denote as the “RPA” kernel in Table I due to the absence of exchange contributions in this block.

To assess the electron–nucleus correlation energy, we use the three RPA variants defined earlier, as listed in Table I, together with MP2. Using the vertex-corrected kernel Γ [Eq. (46)] for the electron–electron block is prohibitively expensive and, therefore, not considered; dRPA or the diagonal approximation is used instead. As MP2 can be exactly partitioned into electron–electron, nucleus–nucleus, and electron–nucleus parts, no further distinction analogous to Table I is needed in this case.

IV. RESULTS

A. Electron–nucleus correlation energies

Table II shows the electron–nucleus correlation energies obtained at the RPA@CHYF level of theory for the species containing ^{13}C . Three different schemes were used to evaluate the correlation energies. The first line of results uses dRPA for both the electrons and the quantum nuclei. The second row uses dRPA for the electrons as well but contains the full vertex contributions from the adiabatic exchange-correlation kernel for the quantum nuclei. The third line treats the quantum nuclei in the same manner while diagonalizing the matrix for the electrons. Figure 1 compares the results of the three RPA methods visually. MP2 calculations were performed as reference calculations to confirm the results. In general, the full dRPA yields correlation energies of the lowest magnitude, which is in contrast to standard electronic dRPA results, which often overestimate correlation.^{54,55} This trend has been observed before for electron–proton correlation,¹⁷ where the MP2 correlation energy is substantially larger than the dRPA one. This trend is also confirmed for the electron– ^{13}C correlation, and Table II demonstrates that indeed MP2 yields correlation energies $\sim 10\%$ larger than dRPA. The overly small dRPA results are an artifact of the large self-interaction error in the nuclear density part, leading to excessively large eigenvalues Ω^{unc} in Eq. (21). Subsequently, the Coulomb coupling in Eq. (20) is overestimated, leading to lower-than-expected coupled eigenvalues Ω and incomplete error cancellation in the final electron– ^{13}C correlation energy. Correlation energies obtained from diag+ Γ for the quantum nuclei are the most negative ones, which is

TABLE II. Calculated electron- ^{13}C correlation energies for ^{13}C , $^{13}\text{CH}_4$, $^{13}\text{CClH}_3$, $^{13}\text{CCl}_3\text{H}$, $^{13}\text{CCl}_4$, $^{13}\text{CCl}_3\text{F}$, and $^{13}\text{CH}_2\text{ClF}$ at the RPA@CHYF and MP2@HF levels of theory. The nucdef-6Z basis set was assigned to the carbon quantum nucleus, while the carbon electrons were computed using the decontracted aug-cc-pV6Z. For the electrons of the remaining elements, the def2-QZVP basis set was employed. The nucdef-6Z basis set was chosen as the auxiliary basis set for carbon, while the other atoms were assigned the def2-QZVP basis set. All values are given in mHartree.

	^{13}C	$^{13}\text{CH}_4$	$^{13}\text{CClH}_3$	$^{13}\text{CCl}_3\text{H}$	$^{13}\text{CCl}_4$	$^{13}\text{CCl}_3\text{F}$	$^{13}\text{CH}_2\text{ClF}$
dRPA	-4.719	-4.832	-4.609	-4.658	-4.543	-4.685	-4.654
dRPA+ Γ	-4.933	-5.053	-4.815	-4.894	-4.772	-4.894	-4.866
diag+ Γ	-5.116	-5.243	-5.036	-5.046	-4.988	-5.044	-5.031
MP2	-5.103	-5.155	-4.920	-4.920	-5.153	-5.151	-5.153

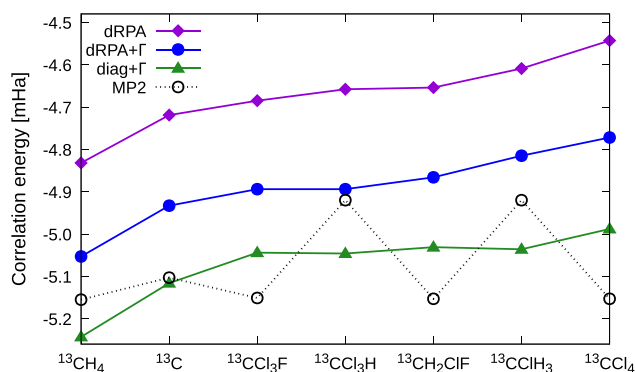


FIG. 1. Calculated electron- ^{13}C correlation energies for ^{13}C , $^{13}\text{CH}_4$, $^{13}\text{CClH}_3$, $^{13}\text{CCl}_3\text{H}$, $^{13}\text{CCl}_4$, $^{13}\text{CCl}_3\text{F}$, and $^{13}\text{CH}_2\text{ClF}$ at the RPA@CHYF and MP2@HF levels of theory for the dRPA (purple squares), dRPA+ Γ (blue circles), diag+ Γ (green triangles), and MP2 (black circles) approximations. All values in mHartree.

in line with the derivation shown in Sec. II B, where it was shown that MP2 and the diagonal approximation in the RPA are related. As the ^{13}C nuclear density is highly localized, the vertex correction arising from $\mathbf{F}^{\text{XC}}$ mainly cancels the Coulomb part. $\mathbf{F}^{\text{XC}}$ is dominated by the exact exchange contributions arising from the CHYF functional. Inspection of the matrix elements of the $\mathbf{A}''$ matrix indeed suggests the latter to be strongly diagonally dominant. The main difference between diag+ Γ @CHYF and MP2@HF, therefore, arises from the different reference states. This has been confirmed by MP2@CHYF calculations, which yield basically identical results, with deviations of only 0.01–0.03 mHartree. The dRPA+ Γ variant falls in between. It provides a balance between the electron correlation and the fully vertex-corrected response of the nuclear density. Most importantly, this variant mitigates the large self-interaction error obtained by a dRPA description of the nucleus, avoiding the over-cancellation effect of the latter. At the same time, due to the coupling between the electronic and nuclear density parts, the influence of fluctuations in the electron density on the nuclear density is already recovered. We therefore deem this variant to be the most accurate one.

For the ^{13}C nucleus, the effect of the chemical environment is still significant and can largely be explained by chemical intuition. $^{13}\text{CH}_4$ exhibits the largest (most negative) electron- ^{13}C correlation

energy, due to a slight increase in electron density provided by the hydrogen atoms. The bare ^{13}C atom lies between $^{13}\text{CH}_4$ and the halogenated species, and the addition of halogen substituents accordingly decreases the correlation energy due to the slightly reduced electron density available at the nucleus. However, these effects are small compared to those observed for hydrogen nuclei,¹⁷ as the 1s core orbitals of ^{13}C do not significantly contribute to bonding. Conversely, chlorine is more electronegative than hydrogen, which reduces the electron density around the carbon nucleus in $^{13}\text{CCl}_4$, resulting in less electron-nucleus correlation. The differences between various halogenation patterns are relatively subtle; however, asymmetric species such as $^{13}\text{CCl}_3\text{F}$ and $^{13}\text{CH}_2\text{ClF}$ exhibit slightly larger correlation energies than the highly symmetric $^{13}\text{CCl}_4$. All tested RPA variants yield the same trend for ^{13}C . In contrast, MP2@HF predicts a loss in correlation energy when hydrogens are attached to the carbon atom, as shown in Table II and Fig. 1. This is indeed counterintuitive, as we would expect fluorine and chlorine to be more efficient at depleting electron density from the carbon nucleus, but HF fails to capture this in the reference state.

For ^{19}F , as shown in Table III and plotted in Fig. 2, the electron- ^{19}F correlation energy gets larger in magnitude due to the more compact 1s orbital, induced by the higher charge. This contraction leads to an increase in magnitude but also to a flatter distribution between different molecular systems. Comparing the correlation energies of ^{19}F and $^{19}\text{F}^-$, the $^{19}\text{F}^-$ electron-nucleus correlation energy has a lower magnitude, even though it features an additional electron. The increased diffuseness of the anion therefore leads to a decrease in the electron- ^{19}F correlation. Notably, both pure dRPA and diag+ Γ -RPA have problems in describing the correlation for the $\text{CCl}_3^{19}\text{F}$ molecule, as indicated by Fig. 2. Only the dRPA+ Γ variant remedies this issue, removing the artificially low correlation energy in this case. MP2@HF, on the other hand, yields results close to diag+ Γ @CHYF, which is to be expected given the relation between these two methods outlined in Sec. II B. For the chlorinated species $\text{CCl}_3^{19}\text{F}$ and $\text{CH}_2\text{Cl}^{19}\text{F}$, however, more pronounced differences are observed, which we attribute to the inability of the Hartree-Fock reference to describe the intrinsic correlation effects in the electron density.

Finally, the influence of scalar relativistic effects on the electron- ^{19}F correlation has been calculated and is shown in Table IV. Scalar relativity leads to a contraction of the 1s orbitals, which in turn leads to an increase in the magnitude of the electron- ^{19}F correlation energy. The increase is on the order of 4%–5%, but all

TABLE III. Calculated electron- ^{19}F correlation energies for ^{19}F , $^{19}\text{F}^-$, $^{19}\text{F}_2$, H^{19}F , $\text{CCl}_3^{19}\text{F}$, and $\text{CH}_2\text{Cl}^{19}\text{F}$ at the RPA@CHYF and MP2@HF levels of theory. The nucdef-6Z basis set was assigned to the fluorine quantum nucleus, while the fluorine electrons were computed using the decontracted aug-cc-pV6Z. For the electrons of the remaining elements, the def2-QZVP basis set was employed. The F_2 value denotes the correlation energy per F nucleus. All values are given in mHartree.

	^{19}F	$^{19}\text{F}^-$	$^{19}\text{F}_2$	H^{19}F	$\text{CCl}_3^{19}\text{F}$	$\text{CH}_2\text{Cl}^{19}\text{F}$
dRPA	-6.053	-5.966	-5.977	-5.955	-5.810	-5.844
dRPA+ Γ	-6.288	-6.198	-6.212	-6.187	-6.148	-6.089
diag+ Γ	-6.487	-6.391	-6.431	-6.390	-6.246	-6.378
MP2	-6.456	-6.443	-6.446	-6.348	-6.444	-6.443

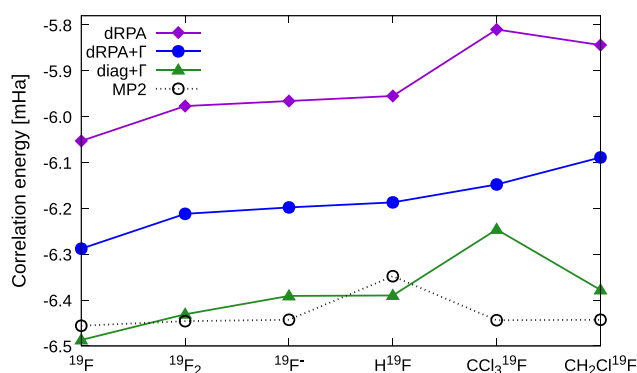


FIG. 2. Calculated electron- ^{19}F correlation energies for ^{19}F , $^{19}\text{F}^-$, $^{19}\text{F}_2$, H^{19}F , $\text{CCl}_3^{19}\text{F}$, and $\text{CH}_2\text{Cl}^{19}\text{F}$ at the RPA@CHYF and MP2@HF levels of theory for the dRPA (purple squares), dRPA+ Γ (blue circles), diag+ Γ (green triangles), and MP2 (black circles) approximations. All values in mHartree.

TABLE IV. Calculated electron- ^{19}F correlation energies for ^{19}F , Au^{19}F , and Tl^{19}F at the X2C-RPA@CHYF and MP2@HF levels of theory. The nucdef-6Z basis set was assigned to the fluorine quantum nucleus, while the fluorine electrons were computed using the decontracted aug-cc-pV6Z basis set. For the electrons of the remaining elements, the x2c-TZVPPall-2c basis set was employed. All values are given in mHartree.

	^{19}F	Au^{19}F	Tl^{19}F
dRPA	-6.300	-6.198	-6.207
dRPA+ Γ	-6.545	-6.451	-6.447
diag+ Γ	-6.757	-6.662	-6.673
MP2	-6.724	-6.686	-6.686

further trends observed previously are preserved. The bare ^{19}F atom still has the largest magnitude, with the Au^{19}F and Tl^{19}F fluorides exhibiting the expected 0.1 mHartree decrease in correlation energy, as also previously observed for H^{19}F .

B. Removing a nucleus from molecular systems

As initially demonstrated in Ref. 17 for hydrogen nuclei, GW can be used to calculate deprotonation energies. Similarly, GW

can be used to calculate the energy needed to remove the ^{13}C and ^{19}F nuclei from molecular systems. Tables V and VI show the respective quasiparticle energies obtained at various levels of GW theory. Specifically, we compare the one-shot G_0W_0 variant using dRPA response and dRPA+ Γ response, as well as the partially self-consistent evGW with dRPA+ Γ response. It is immediately obvious that neglecting the vertex correction leads to sizable errors due to the large self-interaction error in the self-energy Σ^C , which exceeds 5000 eV for both nuclei. Introducing vertex corrections reduces this by a few thousand eV—we explicitly stress that this is not a typo.

Performing dRPA-based GW calculations, which is the de facto standard in electronic GW calculations, leads to catastrophic errors in multicomponent calculations due to the significance of self-interaction errors. A further discussion of these dRPA-based G_0W_0 results is therefore neither needed nor meaningful within the context of this study. evGW is rendered impossible, as the large self-energy correction will lead to a breakdown of the Aufbau principle, especially in the case of ^{13}C nuclei as indicated by the positive sign of ϵ^{QP} in Table V. The vertex correction outlined in Sec. II A by design removes the self-interaction error if the underlying functional is correct for any one-particle density. The latter aspect is crucial and also demonstrates that HF may be preferable to many density functional approximations in this respect. HF, however, suffers from the absence of electron correlation, which, as we have already shown, results in an incorrect ordering of correlation energies, particularly in the case of fluorine nuclei. This leaves one with a limited number of choices for reference densities that can reasonably be used in a multicomponent GW approach. The dRPA+ Γ -based G_0W_0 and evGW results bracket the reference quantum Monte Carlo energy of 2713.8 eV⁵⁶ and the one obtained by summing all ionization energies (2715.9 eV) for the fluorine atom,^{57,58} outlining that the vertex correction is indeed working as intended. Table VI further shows that removing a fluorine nucleus becomes easier once it is part of a chemical system. This can be understood by noting that its removal leaves behind a highly charged system. While removing the nucleus is energetically unfavorable in all investigated systems, the additional nuclei in molecular environments help stabilize the surplus electrons compared to the free atom. The highly charged Au and Tl nuclei are especially “effective” in this respect, while a single hydrogen atom in H^{19}F shows the least stabilizing effect. For carbon, the chemical bonding situation is rather different. Carbon commonly occupies a central spot in the investigated molecules, and removing it from there is generally more favorable if it is surrounded by electronegative bonding partners. Table V even suggests that this effect is enhanced by chlorine bonding partners, with ϵ^{QP} growing from $^{13}\text{CH}_4$ to $^{13}\text{CClH}_3$ to $^{13}\text{CCl}_3\text{H}$ to $^{13}\text{CCl}_4$. Fluorine is better suited to stabilize additional charge than chlorine. The results for the carbon atom itself should be treated with caution, as its electronic structure is relatively complex due to its multideterminant character, which likely leads to larger deviations than those observed in closed-shell compounds. The sum of all ionization energies would amount to 1030.1 eV.⁵⁸ The quasiparticle energy ϵ^{QP} of the free ^{13}C atom significantly overestimates this value. As a final remark, we note that Koopmans’ theorem, which has been demonstrated as working reasonably well for hydrogen nuclei,⁵⁹ is no longer compatible with heavier nuclei. The HF and KS orbital energies are again overestimated by more than 1000 eV, requiring significant quasiparticle

TABLE V. Calculated quasiparticle energies with $Z = 1$ for ^{13}C , $^{13}\text{CH}_4$, $^{13}\text{CClH}_3$, $^{13}\text{CCl}_3\text{H}$, $^{13}\text{CCl}_4$, $^{13}\text{CCl}_3\text{F}$, and $^{13}\text{CH}_2\text{ClF}$ at the GW@CHYF level of theory. The nucdef-6Z basis set was assigned to the carbon quantum nucleus, while the carbon electrons were computed using the decontracted aug-cc-pV6Z. For the electrons of the remaining elements, the def2-QZVP basis set was employed. All values are given in eV.

		^{13}C	$^{13}\text{CH}_4$	$^{13}\text{CClH}_3$	$^{13}\text{CCl}_3\text{H}$	$^{13}\text{CCl}_4$	$^{13}\text{CCl}_3\text{F}$	$^{13}\text{CH}_2\text{ClF}$
dRPA	$\Sigma^{\text{C}} (G_0 W_0)$	5293.54	5529.47	5358.11	5384.66	5426.76	5385.80	5352.20
dRPA+ Γ	$\Sigma^{\text{C}} (G_0 W_0 + \Gamma)$	1279.65	1340.89	1356.10	1387.33	1402.36	1387.07	1352.79
dRPA+ Γ	$\Sigma^{\text{C}} (\text{evGW} + \Gamma)$	1223.14	1314.14	1320.72	1343.29	1357.61	1341.97	1311.50
dRPA	$\epsilon^{\text{QP}} (G_0 W_0)$	2929.08	3148.04	2989.54	3038.65	3091.08	3054.22	2998.52
dRPA+ Γ	$\epsilon^{\text{QP}} (G_0 W_0 + \Gamma)$	-1084.81	-1040.54	-1012.47	-958.68	-933.33	-944.51	-1000.89
dRPA+ Γ	$\epsilon^{\text{QP}} (\text{evGW} + \Gamma)$	-1141.32	-1067.29	-1047.85	-1002.72	-978.08	-989.60	-1042.18

TABLE VI. Calculated quasiparticle energies with $Z = 1$ for ^{19}F , $^{19}\text{F}^-$, $^{19}\text{F}_2$, H^{19}F , $\text{CCl}_3^{19}\text{F}$, $\text{CH}_2\text{Cl}^{19}\text{F}$, Au^{19}F , and Ti^{19}F at the GW@CHYF level of theory. The nucdef-6Z basis set was assigned to the fluorine quantum nucleus, while the fluorine electrons were computed using the decontracted aug-cc-pV6Z. The x2c-TZVPPall basis set was assigned to Au and Ti. For the electrons of the remaining elements, the def2-QZVP basis set was employed. All values are given in eV.

		^{19}F	$^{19}\text{F}^-$	$^{19}\text{F}_2$	H^{19}F	$\text{CCl}_3^{19}\text{F}$	$\text{CH}_2\text{Cl}^{19}\text{F}$	$\text{Au}^{19}\text{F} (\text{X2C})$	$\text{Ti}^{19}\text{F} (\text{X2C})$
dRPA	$\Sigma^{\text{C}} (G_0 W_0)$	4991.72	5282.15	5106.05	5072.69	5219.11	5178.57	5316.31	5319.39
dRPA+ Γ	$\Sigma^{\text{C}} (G_0 W_0 + \Gamma)$	3740.36	4069.51	3882.69	3862.04	4006.99	3965.89	4132.06	4134.97
dRPA+ Γ	$\Sigma^{\text{C}} (\text{evGW} + \Gamma)$	3605.06	4009.27	3721.68	3759.61	3893.57	3851.76	3994.98	4019.19
dRPA	$\epsilon^{\text{QP}} (G_0 W_0)$	-1433.31	-1363.77	-1313.75	-1372.56	-1210.49	-1261.63	-1176.10	-1189.54
dRPA+ Γ	$\epsilon^{\text{QP}} (G_0 W_0 + \Gamma)$	-2684.67	-2481.82	-2537.22	-2583.21	-2422.61	-2474.31	-2360.35	-2373.96
dRPA+ Γ	$\epsilon^{\text{QP}} (\text{evGW} + \Gamma)$	-2819.97	-2542.06	-2698.23	-2685.64	-2536.04	-2588.45	-2497.43	-2489.74

corrections that are three orders of magnitude larger than those observed for valence or core electrons.^{60,61} In light of these results, it is worth questioning whether applying Koopmans' theorem to protons is truly justified.

V. CONCLUSION

We have derived a correlation energy expression generally valid for the interaction of electrons with fermionic nuclei. Based on the random-phase approximation, this approach provides a robust method to assess these kinds of interactions. Similar to standard electronic RPA, the plasmonic formulas remain valid, and the correlation energy can be obtained as the difference between the interacting and non-interacting fermionic systems. Furthermore, a unique connection between minimally coupled RPA and second-order perturbation theory for the inter-fermion correlation has been derived. The latter is only valid in this special context, but we assume it to be theoretically valuable for density functional design, as it allows for the direct inclusion of perturbation theory on general fermion (density) functionals. Our numerical studies of the correlation between electrons and fermionic ^{13}C and ^{19}F nuclei reveal that the correlation energy depends only slightly on the chemical environment, with the heavier ^{19}F nucleus being less sensitive overall. Still, the higher nuclear charge of ^{19}F leads to an enlarged magnitude of the correlation energy overall, outlining that the denser distribution of electrons outweighs the denser packing of the nuclear density distribution. Scalar relativistic effects on the correlation energy are found to again increase the magnitude of the correlation energy by 4%–5%

for the ^{19}F nucleus due to the contraction of the electron density around the nucleus. Numerical GW simulations have proven to be possible, and we have shown that reasonable results can be obtained if vertex corrections are used. Otherwise, self-interaction errors become severe and will distort the results by up to a few thousand eV, rendering them useless. Finally, the large self-energy corrections indicate that previous attempts to apply Koopmans' theorem to nuclear wave functions should be avoided.

SUPPLEMENTARY MATERIAL

The coordinates of the optimized geometries as ASCII XYZ files, ASCII files containing the nucdef-6Z basis sets for carbon and fluorine in Turbomole format, and ASCII files with the generated auxiliary basis sets are contained in the [supplementary material](#).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Janina Vohdin: Data curation (lead); Formal analysis (equal); Investigation (lead); Methodology (supporting); Software (lead); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Christof Holzer:** Conceptualization (lead);

Data curation (supporting); Formal analysis (equal); Investigation (supporting); Methodology (lead); Software (supporting); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

REFERENCES

- ¹M. Born and R. Oppenheimer, “Zur quantentheorie der molekeln,” *Ann. Phys.* **389**, 457–484 (1927).
- ²N. M. Tubman, I. Klyanpää, S. Hammes-Schiffer, and D. M. Ceperley, “Beyond the Born–Oppenheimer approximation with quantum Monte Carlo methods,” *Phys. Rev. A* **90**, 042507 (2014).
- ³C. Li, R. Requist, and E. K. U. Gross, “Density functional theory of electron transfer beyond the Born–Oppenheimer approximation: Case study of LiF,” *J. Chem. Phys.* **148**, 084110 (2018).
- ⁴G. Kolesov, E. Kaxiras, and E. Manousakis, “Density functional theory beyond the Born–Oppenheimer approximation: Accurate treatment of the ionic zero-point motion,” *Phys. Rev. B* **98**, 195112 (2018).
- ⁵C. Holzer and Y. J. Franzke, “A general and transferable local hybrid functional for electronic structure theory and many-fermion approaches,” *J. Chem. Theory Comput.* **21**, 202–217 (2025).
- ⁶J. P. Perdew, A. Ruzsinszky, J. Sun, and K. Burke, “Gedanken densities and exact constraints in density functional theory,” *J. Chem. Phys.* **140**, 18A533 (2014).
- ⁷J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- ⁸J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, “Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids,” *Phys. Rev. Lett.* **91**, 146401 (2003).
- ⁹C. J. Umrigar and X. Gonze, “Accurate exchange–correlation potentials and total-energy components for the helium isoelectronic series,” *Phys. Rev. A* **50**, 3827–3837 (1994).
- ¹⁰E. Matsushita, “Model of electron–proton correlation in quasi-one-dimensional halogen-bridged mixed-valence complexes: Role of proton motion,” *Phys. Rev. B* **51**, 17332–17337 (1995).
- ¹¹M. V. Pak and S. Hammes-Schiffer, “Electron–proton correlation for hydrogen tunneling systems,” *Phys. Rev. Lett.* **92**, 103002 (2004).
- ¹²C. Swalina, M. V. Pak, and S. Hammes-Schiffer, “Alternative formulation of many-body perturbation theory for electron–proton correlation,” *Chem. Phys. Lett.* **404**, 394–399 (2005).
- ¹³C. Swalina, M. V. Pak, A. Chakraborty, and S. Hammes-Schiffer, “Explicit dynamical electron–proton correlation in the nuclear-electronic orbital framework,” *J. Phys. Chem. A* **110**, 9983–9987 (2006).
- ¹⁴A. Sirjoosingh, M. V. Pak, and S. Hammes-Schiffer, “Multicomponent density functional theory study of the interplay between electron–electron and electron–proton correlation,” *J. Chem. Phys.* **136**, 174114 (2012).
- ¹⁵K. R. Brorsen, P. E. Schneider, and S. Hammes-Schiffer, “Alternative forms and transferability of electron–proton correlation functionals in nuclear-electronic orbital density functional theory,” *J. Chem. Phys.* **149**, 044110 (2018).
- ¹⁶Z. Tao, Y. Yang, and S. Hammes-Schiffer, “Multicomponent density functional theory: Including the density gradient in the electron–proton correlation functional for hydrogen and deuterium,” *J. Chem. Phys.* **151**, 124102 (2019).
- ¹⁷C. Holzer and Y. J. Franzke, “Beyond electrons: Correlation and self-energy in multicomponent density functional theory,” *ChemPhysChem* **25**, e202400120 (2024).
- ¹⁸Z. Chen and J. Yang, “Nucleus–electron correlation revising molecular bonding fingerprints from the exact wavefunction factorization,” *J. Chem. Phys.* **155**, 104111 (2021).
- ¹⁹K.-C. Liao, C. M. Bowers, H. J. Yoon, and G. M. Whitesides, “Fluorination, and tunneling across molecular junctions,” *J. Am. Chem. Soc.* **137**, 3852–3858 (2015).
- ²⁰A. Nandi, A. Sucher, and S. Kozuch, “Ping–pong tunneling reactions: Can fluoride jump at absolute zero?,” *Chem.–Eur. J.* **24**, 16348–16355 (2018).
- ²¹C. M. Nunes, A. K. Eckhardt, I. Reva, R. Fausto, and P. R. Schreiner, “Competitive nitrogen versus carbon tunneling,” *J. Am. Chem. Soc.* **141**, 14340–14348 (2019).
- ²²C. Müller, F. Bader, F. A. Redeker, L. Conrad, H. Beckers, B. Paulus, S. Riedel, and J. C. Tremblay, “Experimental observation of quantum mechanical fluorine tunnelling,” *Nat. Commun.* **16**, 4027 (2025).
- ²³J. Messud, “Generalization of internal density-functional theory and Kohn–Sham scheme to multicomponent self-bound systems, and link with traditional density-functional theory,” *Phys. Rev. A* **84**, 052113 (2011).
- ²⁴K. R. Brorsen, Y. Yang, and S. Hammes-Schiffer, “Multicomponent density functional theory: Impact of nuclear quantum effects on proton affinities and geometries,” *J. Phys. Chem. Lett.* **8**, 3488–3493 (2017).
- ²⁵Q. Yu and S. Hammes-Schiffer, “Nuclear-electronic orbital multistate density functional theory,” *J. Phys. Chem. Lett.* **11**, 10106–10113 (2020).
- ²⁶F. Pavošević, T. Culpitt, and S. Hammes-Schiffer, “Multicomponent quantum chemistry: Integrating electronic and nuclear quantum effects via the nuclear-electronic orbital method,” *Chem. Rev.* **120**, 4222–4253 (2020).
- ²⁷S. Hammes-Schiffer, “Nuclear-electronic orbital methods: Foundations and prospects,” *J. Chem. Phys.* **155**, 030901 (2021).
- ²⁸M. Goli and S. Shahbazian, “Two-component density functional theory for muonic molecules: Inclusion of the electron–positive muon correlation functional,” *J. Chem. Phys.* **156**, 044104 (2022).
- ²⁹T. Kreibich and E. K. U. Gross, “Multicomponent density-functional theory for electrons and nuclei,” *Phys. Rev. Lett.* **86**, 2984–2987 (2001).
- ³⁰A. Chakraborty, M. V. Pak, and S. Hammes-Schiffer, “Development of electron–proton density functionals for multicomponent density functional theory,” *Phys. Rev. Lett.* **101**, 153001 (2008).
- ³¹T. Kreibich, R. van Leeuwen, and E. K. U. Gross, “Multicomponent density-functional theory for electrons and nuclei,” *Phys. Rev. A* **78**, 022501 (2008).
- ³²G. P. Chen, V. K. Voora, M. M. Agee, S. G. Balasubramani, and F. Furche, “Random-phase approximation methods,” *Annu. Rev. Phys. Chem.* **68**, 421–445 (2017).
- ³³S. P. Webb, T. Iordanov, and S. Hammes-Schiffer, “Multiconfigurational nuclear-electronic orbital approach: Incorporation of nuclear quantum effects in electronic structure calculations,” *J. Chem. Phys.* **117**, 4106–4118 (2002).
- ³⁴F. Furche, “Molecular tests of the random phase approximation to the exchange–correlation energy functional,” *Phys. Rev. B* **64**, 195120 (2001).
- ³⁵D. C. Langreth and J. P. Perdew, “Exchange–correlation energy of a metallic surface: Wave-vector analysis,” *Phys. Rev. B* **15**, 2884–2901 (1977).
- ³⁶X. Ren, P. Rinke, C. Joas, and M. Scheffler, “Random-phase approximation and its applications in computational chemistry and materials science,” *J. Mater. Sci.* **47**, 7447–7471 (2012).
- ³⁷C. Holzer, “Practical post-Kohn–Sham methods for time-reversal symmetry breaking references,” *J. Chem. Theory Comput.* **19**, 3131–3145 (2023).
- ³⁸T. Olsen, C. E. Patrick, J. E. Bates, A. Ruzsinszky, and K. S. Thygesen, “Beyond the RPA and GW methods with adiabatic xc-kernels for accurate ground state and quasiparticle energies,” *npj Comput. Mater.* **5**, 106 (2019).
- ³⁹G. E. Scuseria, T. M. Henderson, and D. C. Sorensen, “The ground state correlation energy of the random phase approximation from a ring coupled cluster doubles approach,” *J. Chem. Phys.* **129**, 231101 (2008).
- ⁴⁰J. Almlöf, “Elimination of energy denominators in Møller–Plesset perturbation theory by a Laplace transform approach,” *Chem. Phys. Lett.* **181**, 319–320 (1991).
- ⁴¹M. Häser and J. Almlöf, “Laplace transform techniques in Møller–Plesset perturbation theory,” *J. Chem. Phys.* **96**, 489–494 (1992).
- ⁴²M. Häser, “Møller–Plesset (MP2) perturbation theory for large molecules,” *Theor. Chim. Acta* **87**, 147–173 (1993).
- ⁴³C. Holzer and W. Klopper, “Ionized, electron-attached, and excited states of molecular systems with spin-orbit coupling: Two-component GW and Bethe–Salpeter implementations,” *J. Chem. Phys.* **150**, 204116 (2019).

- ⁴⁴M. J. van Setten, F. Weigend, and F. Evers, "The *gw*-method for quantum chemistry applications: Theory and implementation," *J. Chem. Theory Comput.* **9**, 232–246 (2013).
- ⁴⁵P. Pollak and F. Weigend, "Segmented contracted error-consistent basis sets of double- and triple- ζ valence quality for one- and two-component relativistic all-electron calculations," *J. Chem. Theory Comput.* **13**, 3696–3705 (2017).
- ⁴⁶W. Kutzelnigg and W. Liu, "Quasirelativistic theory equivalent to fully relativistic theory," *J. Chem. Phys.* **123**, 241102 (2005).
- ⁴⁷L. Visscher and K. G. Dyall, "Dirac–Fock atomic electronic structure calculations using different nuclear charge distributions," *At. Data Nucl. Data Tables* **67**, 207–224 (1997).
- ⁴⁸Y. J. Franzke, N. Middendorf, and F. Weigend, "Efficient implementation of one- and two-component analytical energy gradients in exact two-component theory," *J. Chem. Phys.* **148**, 104410 (2018).
- ⁴⁹S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Voora, F. Weigend, A. Wodyński, and J. M. Yu, "Turbomole: Modular program suite for *ab initio* quantum-chemical and condensed-matter simulations," *J. Chem. Phys.* **152**, 184107 (2020).
- ⁵⁰Y. J. Franzke, C. Holzer, J. H. Andersen, T. Begušić, F. Bruder, S. Coriani, F. Della Sala, E. Fabiano, D. A. Fedotov, S. Furst, S. Gillhuber, R. Grotjahn, M. Kaupp, M. Kehry, M. Krstić, F. Mack, S. Majumdar, B. D. Nguyen, S. M. Parker, F. Pauly, A. Pausch, E. Perlt, G. S. Phun, A. Rajabi, D. Rappoport, B. Samal, T. Schrader, M. Sharma, E. Tapavicza, R. S. Treß, V. Voora, A. Wodyński, J. M. Yu, B. Zerulla, F. Furche, C. Hättig, M. Sierka, D. P. Tew, and F. Weigend, "Turbomole: Today and tomorrow," *J. Chem. Theory Comput.* **19**, 6859–6890 (2023).
- ⁵¹S. Lehtola, "Straightforward and accurate automatic auxiliary basis set generation for molecular calculations with atomic orbital basis sets," *J. Chem. Theory Comput.* **17**, 6886–6900 (2021).
- ⁵²S. Lehtola, "Automatic generation of accurate and cost-efficient auxiliary basis sets," *J. Chem. Theory Comput.* **19**, 6242–6254 (2023).
- ⁵³J. Lehtola, M. Hakala, A. Sakko, and K. Hämäläinen, "ERKALE—A flexible program package for X-ray properties of atoms and molecules," *J. Comput. Chem.* **33**, 1572–1585 (2012).
- ⁵⁴H. Eshuis, J. E. Bates, and F. Furche, "Electron correlation methods based on the random phase approximation," *Theor. Chem. Acc.* **131**, 1084 (2012).
- ⁵⁵C. Holzer, X. Gui, M. E. Harding, G. Kresse, T. Helgaker, and W. Klopper, "Bethe–Salpeter correlation energies of atoms and molecules," *J. Chem. Phys.* **149**, 144106 (2018).
- ⁵⁶A. Lüchow and J. B. Anderson, "Accurate quantum Monte Carlo calculations for hydrogen fluoride and the fluorine atom," *J. Chem. Phys.* **105**, 4636–4640 (1996).
- ⁵⁷E. Biémont, Y. Frémat, and P. Quinet, "Ionization potentials of atoms and ions from lithium to tin ($Z = 50$)," *At. Data Nucl. Data Tables* **71**, 117–146 (1999).
- ⁵⁸A. Kramida, Y. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (version 5.12), available online: <https://physics.nist.gov/asd>, 2024, accessed 16 April 2026.
- ⁵⁹T. Schrader, J. Khanifaev, and E. Perlt, "Koopmans' theorem for acidic protons," *Chem. Commun.* **59**, 13839–13842 (2023).
- ⁶⁰F. Caruso, M. Dauth, M. J. van Setten, and P. Rinke, "Benchmark of GW approaches for the GW100 test set," *J. Chem. Theory Comput.* **12**, 5076–5087 (2016).
- ⁶¹M. Kehry, W. Klopper, and C. Holzer, "Robust relativistic many-body Green's function based approaches for assessing core ionized and excited states," *J. Chem. Phys.* **159**, 044116 (2023).