

A finite-element Delta-Sternheimer approach for accurate all-electron RPA correlation energies of arbitrary molecules

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The incompleteness of single-particle basis sets has long cast a shadow over correlated electronic-structure methods, making it highly challenging to obtain numerically converged results. In this work, we compute the RPA correlation energies of general molecules using the finite element method, while ingeniously combining atomic orbital basis sets to accelerate the convergence of total energies. We report atomization energies for 50 molecules within the RPA framework, achieving accuracies on the order of meV per atom. The computational strategy that integrates real-space discretization techniques with atomic orbitals is expected to inspire the entire correlated electronic-structure community.

INTRODUCTION

The tremendous success of density functional theory (DFT) has laid a solid foundation for research in quantum chemistry and materials science[1, 2]. In recent years, an increasing number of scientists have devoted their efforts to developing electronic structure methods with higher theoretical accuracy, aiming to better describe the correlation effects between electrons [3–6]. These methods have considerably enriched the toolbox of electronic-structure theory and allow practitioners to choose an approach appropriate to system size and desired accuracy. However, most correlated electronic-structure methods suffer from slow convergence with respect to the single-particle basis set. In configuration interaction (CI) and coupled-cluster (CC) theories[7–9], the N -electron wavefunction is expanded in Slater determinants constructed from single-particle orbitals. Ideally, a complete set of such determinants spans the exact many-body space, but in practice the space is truncated by the incompleteness of the single-particle basis, leading to basis-set errors. Similarly, the random-phase approximation (RPA) and the GW approximation require evaluation of the density–density response function[10, 11], which depends on a complete set of single-particle states; hence, basis-set incompleteness directly affects their accuracy. In GW, the non-interaction Green’s function in the Lehmann representation likewise relies on the full single-particle spectrum. The same reasoning applies to Møller–Plesset second-order perturbation theory (MP2)[12], which can be regarded as the non-self-consistent limit of coupled-cluster doubles (CCD)[9]. Overall, most correlated electronic-structure methods are fundamentally limited by the incompleteness of the single-particle basis.

Consequently, reaching the complete-basis-set (CBS) limit is a central challenge for correlated calculations. A standard and convenient strategy is to use correlation-

consistent Gaussian basis sets developed by Dunning and co-workers and to apply extrapolation formulas to estimate the CBS limit [13, 14]. On the numerical atomic orbital side, NAO-VCC-nZ sets have been introduced to provide correlation-consistent NAOs [15]. Although extrapolation with correlation-consistent basis set often reduces basis errors at modest cost, truly high-accuracy, parameter-free CBS results remain difficult to obtain.

A fundamental source of this difficulty is the electron–electron cusp: owing to the Coulomb singularity the many-electron wavefunction has a Kato cusp when two electrons coincide[16]. Explicitly correlated (R_{12}/F_{12}) approaches introduce interelectronic-distance factors to remove the cusp and thereby dramatically accelerate basis convergence[17–23]; these techniques have been incorporated into CI, MP2, RPA, CC and related methods[21, 24–30]. However, F_{12}/R_{12} methods require many additional electron–electron integrals and can be costly for large systems.

Real-space approaches provide an alternative way to obtain numerically precise result by representing wavefunctions and related quantities directly on a spatial grid or localized real-space basis. The commonly used real-space discretization schemes include the finite-difference method(FDM), the finite-element method(FEM), and the multiresolution wavelet (MRA) approach[31–33]. These methods allow the systematic reduction of discretization errors by controlling a single parameter, enabling the convergence of energies and other physical quantities to arbitrary precision. In recent several decades, achieving numerically exact electronic structure calculations based on real-space methods has become an important and active area of research. For example, Flores obtained highly accurate atomic MP2 correlation energies using the p-version FEM [34, 35]. MRA have been employed to compute correlated energies within coupled-cluster (CC) and second-order Møller–Plesset perturbation theory (MP2)frameworks[36–39]. Numerical precise RPA correlation energies are obtained based on real space

Sternheimer method for atomic and diatomic molecules in our previous work [40, 41]. However, despite these advances, applying real-space methods to correlated many-electron calculations beyond small atoms and dimers remains challenging, primarily due to their expensive computational cost. To address this limitations, hybrid strategies that combine real-space representations with localized atomic-orbital (AO) basis offer a promising pathway toward improved efficiency and scalability. In the FLAPW basis, Markus Betzinger et al. divided the first-order wave function into components inside and outside the basis space[42–44]. Within the basis space, the first-order wave function can still be expanded in terms of the FLAPW basis functions, while outside the basis space, it is obtained by solving for the response of the basis functions on a one-dimensional grid. This approach effectively eliminates the basis-set error of the FLAPW method in computing response functions and also cleverly combines the real-space approach with a finite basis set.

In this work, we extend our real-space RPA framework to general small molecules using the FEM. Inspired by the work of Betzinger et al. [42–44], and the concept of Δ -learning in the field of machine learning[45], we have pioneered a method that combines real-space finite element(FE) techniques with a finite atomic-orbital basis, significantly accelerating the convergence of the energy with respect to the FE grid. We refer to this approach as the Delta-Sternheimer approach. By FE Delta-Sternheimer approach, we obtain numerically converged all-electron RPA atomization energies. This overcomes our previous restriction to atomic and diatomic systems. More importantly, the approach of combining real-space techniques with atomic orbitals holds tremendous application potential. This work is expected to inspire solutions to basis-set error issues in other electronic-structure methods.

RESULTS AND DISCUSSIONS

The essence of the present work lies in correcting the single-particle basis-set errors that commonly affect RPA calculations with finite atomic basis sets. We are therefore particularly interested in how finite single-particle basis sets influence energy differences under RPA. In this section, we present benchmark tests in two aspects. In the first part, we examine the small energy differences between different configurations of the water dimers. We compare results obtained using the conventional finite-basis “sum-over-states” (SOS) method with those obtained in this work using the FE Delta-Sternheimer approach. By testing three widely used correlation-consistent basis sets, we assess the impact of finite single-particle basis-set errors on the calculation of energy differences in the water dimers.

In the second part, we select 50 small molecules containing elements from the first three periods from the G2/97 set [46] and compute their RPA atomization energies. These results are compared with those obtained using the finite-basis SOS approach to evaluate the errors arising from finite basis sets in RPA atomization energy calculations. At the same time, we also compute results extrapolated from correlation-consistent basis sets and, by comparison with our FE results, assess the errors and reliability of the extrapolation approach.

Basis-set-issue check for water dimer

We first applied the present technique to the water dimer, for which the energy differences between different configurations are exceedingly small. Our primary objective is to quantify how well these minute energy differences are reproduced by different single-particle basis sets—that is, to assess the magnitude of the basis-set incompleteness error. To this end, we randomly selected 20 geometries from a 200-step molecular-dynamics trajectory of the water dimer. For each configuration, we performed adaptive mesh refinement in the FE representation to obtain numerically converged AE RPA correlation energies, which we treat as reference RPA values. The Hartree-Fock(HF) total energy (single-particle energies + Hartree + exact exchange) are taken as reference values when computed with the highly converged FHI-aims-2010(*tier*) NAO basis sets [47]. Results to be compared were produced using the SOS approach with three families of correlation-consistent basis sets: (1) aug-cc-pwCVXZ, (2) cc-pVXZ, and (3) NAO-VCC-nZ [48, 49]. Another important point to note is that all calculations in this part were performed using the same auxiliary basis sets. Specifically, we employed the largest RI-fitting basis sets available from the Basis Set Exchange website: aug-cc-pwCV5Z-RIFIT for oxygen and aug-cc-pV6Z-RIFIT for hydrogen. The choice of identical auxiliary basis sets across all calculations was intentional, as our primary focus is on the error introduced by the single-particle basis sets, not the resolution-of-identity (RI) approximation. Furthermore, the use of the largest available RI-fitting basis sets ensures that the RI error remains negligible. We ranked the 20 configurations by total energy computed with the FE Delta-Sternheimer method, from lowest to highest, and set the energy of the lowest-energy configuration to zero, and the energy differences of the other configurations were calculated relative to this reference. We then compared the results obtained with different correlation-consistent basis sets based on SOS method to those obtained using the Delta-Sternheimer method. The result for aug-cc-pwCVXz is shown in the figure below, other results are shown in SM. It is clear that as the basis set size increases, the energy difference curves obtained from the

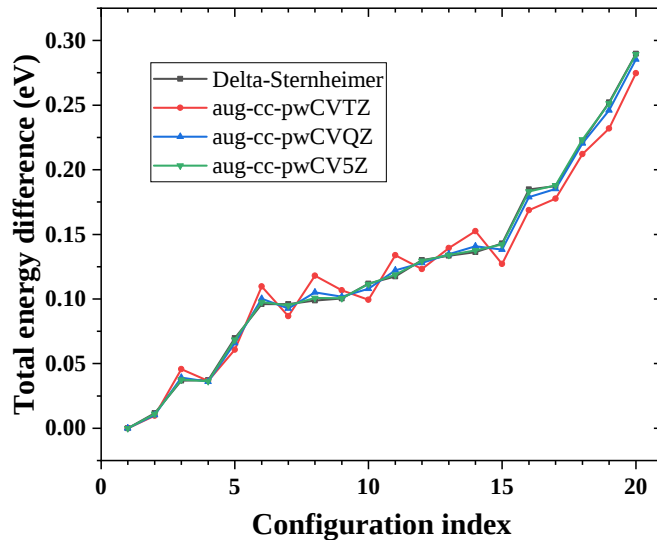


FIG. 1. The RPA total energy differences of 20 different configurations of the water dimer.

three different types of correlation-consistent basis sets gradually approach the reference results from the FE Delta-Sternheimer method. It is readily apparent that the aug-cc-pwCVTZ basis set yields an incorrect total-energy ordering for some configurations; this problem essentially disappears with aug-cc-pwCVQZ and aug-cc-pwCV5Z. Other correlation-consistence basis sets share the similar information in SM. To quantify the basis set error, we calculate,

$$\text{Error} = \sum_{j=2}^{20} \frac{|\Delta_j - \Delta_j^{\text{ref}}|}{19}. \quad (1)$$

Here, $\Delta_j = E_j - E_1$, E_j and E_1 represent the energy of j -th configuration and the lowest-energy configuration. The superscript "ref" denotes the energy obtained from the FE Delta-Sternheimer method, while values without a superscript correspond to the energies calculated using different correlation-consistent basis sets. We can separately calculate the basis set errors for the total energy, the HF total energy, and the RPA correlation energy. The results are shown below (energy unit is meV). Tab. X shows that when all three basis-set families are taken at their largest level, the HF errors are all below 1 meV. This arises because the HF total depends primarily on the description of the occupied-state manifold, so basis-set incompleteness is negligible. For the RPA correlation energy, only the aug-cc-pwCVXZ family converges to within 1 meV, which is likely because the other two families do not explicitly account for core-valence correlation effects.

Atomization energies

Here, we calculated the RPA atomization energies of 50 molecules selected from the G2/97 set. All molecular geometries were taken from Ref. [50]. The computational details are described below. First, we still separate the RPA total energy into the RPA correlation energy and HF total energy. For the latter, we performed calculations in FHI-aims using the aug-cc-pwCV5Z basis set. The error in this part mainly originates from the basis-set incompleteness of the atomic orbitals used to describe the occupied manifold. To evaluate this error at the level of atomization energies, we performed calculations using aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets, and extrapolated the results to the CBS limit using a standard formula(detail see SM),

In addition, calculations with the built-in *tier* basis sets of FHI-aims were also performed for reference. These results are summarized in SM.

From Tab.S9 in SM, it is evident that the results obtained with the aug-cc-pwCV5Z basis set agree very well with both the extrapolated values and those based on the NAO basis. The data in the last row indicate that the HF contribution to the atomization energy obtained with the largest Gaussian basis differs from the extrapolated result by only 0.03 kcal/mol, and from the largest NAO result by just 0.02 kcal/mol. This demonstrates that the aug-cc-pwCV5Z basis set provides a description of the occupied states that is already very close to the CBS limit at the level of atomization energies. It also indicates that the choice of different types of atomic orbitals introduces very little uncertainty in the description of the occupied

Energy part	aug-pwCVXZ			NAO-VCC-nZ			cc-pVXZ		
	TZ	QZ	5Z	3Z	5Z	5Z	QZ	5Z	6Z
RPA	7.01	2.69	0.78	5.85	4.30	1.16	7.49	5.45	3.95
HF	4.24	0.76	0.23	2.36	1.28	0.78	1.97	0.64	0.66
TOTAL	11.24	3.45	0.97	4.83	3.17	1.65	7.27	5.18	4.16

TABLE I. Comparison of basis set error for different basis sets. The energy unit is meV.

states. And these results are consistent with results in the water dimer tests.

For the RPA correlation energy, we solved the Delta-Sternheimer equation in the FE space to obtain the density-response matrix and the correlation energy. The main error sources here can be attributed to three aspects: (1) the FE grid density, (2) the RI approximation, and (3) the effect of basis-set errors in the occupied orbitals and energies on the RPA correlation energy when solving the Delta-Sternheimer equation. Convergence tests for all three sources are provided in the SM. The results show that the errors from the FE grid density and from the occupied-state orbitals and energies are both below the meV level, and thus negligible compared with the RI error. The RI approximation therefore constitutes the dominant source of error in this work. To minimize it, we employed auxiliary bases generated on-the-fly from aug-cc-pwCV5Z with $L_{\max} = 9$. Tests on diatomic molecules indicate that the average error at the level of atomization energies is only 0.04 kcal/mol. Since the RI error is expected to scale linearly with the number of atoms, it can be estimated as about 0.02 kcal/mol per atom. Taken together, after considering all possible error sources, we conclude that the dominant error in this work arises from the RI approximation, amounting to roughly 0.02 kcal/mol per atom. In Tab. XII, we report the total atomization energies of 50 molecules at the RPA level (including both the HF contribution and the RPA correlation contribution). These results can serve as reference data for future benchmarking studies and provide numerical standards for the development of correlation-consistent basis sets. In addition, to assess the basis set errors of finite-basis calculations, we present results obtained with the aug-cc-pwCV5Z basis set within the SOS framework. Furthermore, we report CBS-extrapolated results obtained by applying standard extrapolation formula to the SOS results from aug-cc-pwCVQZ and aug-cc-pwCV5Z, which allow us to evaluate the accuracy of the extrapolation schemes.

From Tab. XII, it can be seen that the basis set error within the finite-basis SOS framework is 1.67 kcal/mol (for AE) and 1.70 kcal/mol (for FC). After extrapolation to the CBS limit using the extrapolation formula, the mean error is reduced to 0.34 kcal/mol (for AE) and 0.33 kcal/mol (for FC). This indicates that the extrapolation technique can indeed effectively reduce the basis set error.

We also observe that the finite-basis results consistently underestimate the atomization energies, whereas the extrapolated results consistently overestimate them. We attribute this to the basis set superposition error (BSSE). In the calculations of Tab. XII, neither the finite-basis nor the extrapolated results account for BSSE, as the atomic energies were computed independently. To examine the influence of BSSE, we selected 10 molecules from Tab. XII and investigated the effect of BSSE on the atomization energies. The results are presented in Tab. S11 in SM. It can be seen that after the CP correction, the tendency of the extrapolated results to overestimate the atomization energies almost disappears. The mean error with respect to the results of this work is slightly reduced. The impact of the CP correction on finite-basis results is much larger than on extrapolated results, with the error increasing from 0.95 kcal/mol to 3.22 kcal/mol. Therefore, based on these results, for finite-basis calculations, the results obtained without the CP correction are more reliable. For results extrapolated to the basis-set limit, the CP correction can slightly improve accuracy.

SUMMARY

In this work, by combining the high efficiency of atomic orbitals with the systematic nature of the finite element method, we developed the FE Delta-Sternheimer approach, which can compute accurate RPA correlation energies for general molecules with a reasonable computational cost. This work not only provides precise RPA atomization energies for 50 small molecules, but also assesses the errors arising from finite basis sets and extrapolation methods. It offers high-accuracy benchmark results and demonstrates the significant potential of integrating real-space techniques with localized atomic orbitals.

METHOD

The key to RPA calculations without single-particle basis set errors is to obtain numerically accurate first-order KS wavefunction (WF) induced by arbitrary external perturbation. To introduce our approach, we start

MO	This work AE	This work FC	5Z AE	5Z FC	Extrapolation AE	Extrapolation FC
CH ₄	-406.10	-404.93	-405.31 (0.79)	-404.17 (0.76)	-406.35 (-0.25)	-405.17 (-0.24)
C ₂ H ₂	-383.47	-381.02	-381.99 (1.49)	-379.61 (1.41)	-383.91 (-0.44)	-381.42 (-0.40)
C ₂ H ₄	-539.70	-537.41	-538.26 (1.44)	-536.04 (1.37)	-540.08 (-0.38)	-537.77 (-0.36)
C ₃ H ₆ (1)	-823.79	-820.43	-821.63 (2.16)	-818.30 (2.12)	-824.35 (-0.56)	-820.90 (-0.47)
C ₃ H ₆ (2)	-816.32	-815.37	-813.92 (2.40)	-810.59 (4.77)	-816.75 (-0.43)	-813.30 (2.07)
C ₃ H ₄ (1)	-668.66	-665.09	-666.58 (2.08)	-663.08 (2.00)	-669.08 (-0.42)	-665.44 (-0.35)
C ₃ H ₄ (2)	-669.82	-666.23	-667.62 (2.20)	-664.09 (2.14)	-670.32 (-0.50)	-666.64 (-0.41)
C ₃ H ₄ (3)	-647.45	-644.04	-645.19 (2.26)	-641.85 (2.19)	-647.88 (-0.42)	-644.40 (-0.36)
C ₂ H ₆	-686.11	-683.89	-684.54 (1.57)	-682.38 (1.51)	-686.51 (-0.40)	-684.26 (-0.37)
CH ₂ O	-356.97	-355.62	-355.69 (1.27)	-354.36 (1.26)	-357.17 (-0.21)	-355.79 (-0.17)
CH ₃ OH	-492.28	-490.92	-490.79 (1.49)	-489.44 (1.48)	-492.57 (-0.29)	-491.18 (-0.26)
CH ₂ O ₂	-475.22	-473.42	-473.18 (2.03)	-471.43 (1.99)	-475.51 (-0.30)	-473.70 (-0.28)
C ₂ H ₂ O ₂	-600.27	-597.52	-597.73 (2.54)	-595.02 (2.50)	-600.63 (-0.36)	-597.81 (-0.30)
C ₂ H ₆ O	-776.84	-774.42	-774.68 (2.16)	-772.25 (2.17)	-777.36 (-0.52)	-774.86 (-0.44)
C ₂ H ₄ O(1)	-646.31	-643.76	-644.21 (2.10)	-641.73 (2.04)	-646.68 (-0.37)	-644.10 (-0.34)
C ₂ H ₄ O(2)	-620.55	-618.25	-618.38 (2.17)	-616.04 (2.21)	-620.92 (-0.36)	-618.49 (-0.24)
H ₂ O	-223.57	-223.26	-222.99 (0.58)	-222.60 (0.66)	-223.90 (-0.34)	-223.51 (-0.25)
H ₂ O ₂	-256.30	-255.78	-255.10 (1.20)	-254.59 (1.19)	-256.48 (-0.18)	-255.98 (-0.20)
CO ₂	-366.44	-364.51	-364.59 (1.85)	-362.61 (1.90)	-366.76 (-0.32)	-364.70 (-0.19)
NH ₃	-291.30	-290.65	-290.54 (0.76)	-289.90 (0.75)	-291.59 (-0.29)	-290.93 (-0.28)
N ₂ H ₄	-427.91	-426.72	-426.26 (1.65)	-425.11 (1.61)	-428.22 (-0.31)	-427.04 (-0.32)
HCN	-300.54	-298.69	-299.19 (1.35)	-297.42 (1.27)	-300.81 (-0.27)	-298.96 (-0.27)
C ₃ NH ₃	-725.79	-721.71	-723.18 (2.61)	-719.15 (2.56)	-726.37 (-0.58)	-722.16 (-0.45)
C ₂ NH ₅	-691.54	-688.80	-689.16 (2.38)	-686.48 (2.32)	-691.95 (-0.41)	-689.18 (-0.38)
CNH ₅	-563.31	-561.65	-561.78 (1.53)	-560.12 (1.53)	-563.74 (-0.43)	-562.03 (-0.38)
C ₂ N ₂	-476.28	-472.61	-473.92 (2.36)	-470.30 (2.31)	-476.78 (-0.50)	-472.99 (-0.38)
N ₂ O	-259.68	-258.10	-257.83 (1.85)	-256.27 (1.82)	-259.84 (-0.16)	-258.24 (-0.14)
CHF ₃	-423.46	-422.28	-421.45 (2.01)	-420.28 (1.99)	-423.58 (-0.12)	-422.38 (-0.10)
C ₂ H ₃ F	-542.26	-539.87	-540.42 (1.84)	-538.08 (1.79)	-542.61 (-0.35)	-540.18 (-0.31)
CH ₂ F ₂	-409.97	-408.89	-408.42 (1.55)	-407.30 (1.59)	-410.19 (-0.22)	-409.04 (-0.15)
NF ₃	-183.91	-183.63	-182.35 (1.56)	-182.02 (1.61)	-183.95 (-0.04)	-183.64 (-0.01)
C ₂ H ₃ OF	-667.47	-664.80	-665.00 (2.47)	-662.38 (2.42)	-667.86 (-0.39)	-665.15 (-0.35)
F ₂ O	-78.95	-78.79	-77.96 (0.99)	-77.78 (1.01)	-78.98 (-0.03)	-78.81 (-0.02)
COF ₂	-386.78	-385.16	-384.65 (2.13)	-383.02 (2.14)	-386.92 (-0.15)	-385.25 (-0.09)
C ₃ H ₈	-967.94	-964.66	-965.64 (2.30)	-962.43 (2.23)	-968.52 (-0.58)	-965.19 (-0.53)
C ₆ H ₆	-1298.40	-1291.33	-1293.79 (4.61)	-1286.95 (4.38)	-1299.02 (-0.62)	-1291.92 (-0.59)
H ₂ S	-177.79	-177.06	-177.56 (0.23)	-176.87 (0.19)	-177.83 (-0.03)	-177.17 (-0.11)
CS ₂	-263.41	-260.62	-261.92 (1.49)	-259.40 (1.22)	-263.80 (-0.39)	-261.27 (-0.65)
CH ₄ S	-456.48	-454.85	-455.61 (0.87)	-453.92 (0.93)	-456.91 (-0.43)	-455.25 (-0.40)
COS	-315.45	-313.28	-314.02 (1.43)	-311.79 (1.49)	-315.97 (-0.52)	-313.68 (-0.40)
SO ₂	-243.33	-241.90	-241.49 (1.84)	-240.03 (1.87)	-243.69 (-0.36)	-242.25 (-0.35)
HClO	-155.02	-154.56	-154.18 (0.84)	-153.68 (0.88)	-155.16 (-0.14)	-154.69 (-0.13)
CH ₃ Cl	-377.24	-375.96	-376.33 (0.91)	-374.97 (0.99)	-377.61 (-0.37)	-376.25 (-0.29)
NOCl	-181.15	-180.24	-179.82 (1.33)	-178.91 (1.33)	-181.21 (-0.06)	-180.29 (-0.05)
CH ₂ Cl ₂	-347.74	-346.32	-346.76 (0.98)	-345.12 (1.20)	-348.21 (-0.47)	-346.61 (-0.29)
C ₂ H ₃ Cl	-514.50	-511.94	-512.92 (1.58)	-510.36 (1.58)	-514.98 (-0.48)	-512.37 (-0.43)
C ₂ NH ₃	-589.88	-586.93	-587.85 (2.03)	-584.93 (2.00)	-590.30 (-0.42)	-587.26 (-0.33)
SiH ₄	-316.27	-315.57	-316.10 (0.17)	-315.38 (0.19)	-316.57 (-0.30)	-315.94 (-0.36)
PH ₃	-239.39	-238.70	-239.30 (0.09)	-238.55 (0.15)	-239.60 (-0.22)	-238.93 (-0.23)
BF ₃	-435.64	-433.21	-433.51 (2.12)	-431.27 (1.94)	-436.08 (-0.45)	-433.49 (-0.28)
MAE	/	/	1.67	1.70	0.34	0.33

TABLE II. The atomization energies of 50 molecules at the RPA level (including the EXX contribution and the RPA correlation part) are reported. The second and third columns represent the AE and FC approximation atomization energies obtained in this work. The fourth and fifth columns show the AE and FC approximation atomization energies calculated with the aug-cc-pwCV5Z basis set. The sixth and seventh columns correspond to the extrapolated results obtained from the aug-cc-pwCVQZ and aug-cc-pwCV5Z data. The energies are given in kcal/mol.

with the KS Hamiltonian $H^{(0)}$,

$$H^{(0)} = -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \quad (2)$$

where $v_{\text{eff}}(\mathbf{r})$ is the KS effective potential. Upon adding a small frequency-dependent perturbation $V^{(1)}(\mathbf{r})e^{i\omega t}$ to the Hamiltonian $H^{(0)}$, the linear response of the system

is governed by the following frequency-dependent Sternheimer equation [40],

$$(H^{(0)} - \epsilon_i + i\omega)\psi_i^{(1)}(\mathbf{r}, i\omega) = (\epsilon_i^{(1)} - V^{(1)})\psi_i(\mathbf{r}), \quad (3)$$

where $\psi_i(\mathbf{r})$ and ϵ_i are the KS orbitals and orbital energies, and $\psi_i^{(1)}(\mathbf{r}, i\omega)$ and $\epsilon_i^{(1)}$ are their first-order variations, respectively. In our previous work [40,

41], we solved Eq. 24 using real-space finite difference methods on one-dimensional logarithmic grids and two-dimensional prolate spheroidal grids. By systematically increasing the grid density, the discretization error from the real-space representation could be reliably converged. This enabled the calculation of AE RPA correlation energies for atoms and diatomic molecules without basis-set-error.

However, for general molecular systems—as considered in this work—the finite-difference method (FDM) becomes increasingly impractical. The main difficulty arises from the loss of symmetry: in contrast to atoms or diatomic molecules, three-dimensional molecular systems require grid points distributed along all spatial directions. Experience with two-dimensional prolate spheroidal grids indicates that roughly 200 points are typically required along each axis. Extending this to three dimensions results in about 8 million grid points in total, leading to an unmanageable computational cost.

For atoms and diatomic molecules, the one-dimensional logarithmic grid and the two-dimensional prolate spheroidal grid both feature non-uniform point distributions—dense near the nuclei, where the wavefunction varies rapidly, and sparse in the outer regions, where it changes smoothly. This design enables efficient all-electron calculations: the fine grid near the nuclei captures the rapid oscillations of the wavefunction, while fewer points are used in the asymptotic region. Moreover, both grid types allow coordinate transformations that map the non-uniform physical grid to a uniform virtual grid, on which standard finite-difference derivatives can be evaluated conveniently.

An ideal coordinate system for real-space grid methods should therefore meet three requirements: (1) it must accurately resolve the wavefunction behavior near nuclei; (2) it should allow a transformation to a uniform virtual grid suitable for finite-difference operations; and (3) it must be computationally efficient, keeping the total number of grid points manageable.

Unfortunately, no known three-dimensional coordinate system satisfies all three conditions simultaneously. Consequently, we do not pursue the real-space finite-difference approach further. Instead, we seek an alternative real-space discretization method that is more suitable for general molecular systems.

In this context, the finite-element method (FEM) provides an attractive solution. FEM divides real space into a set of small elements and defines local basis functions—finite-element shape functions—within each element. Any continuous function can then be represented as a linear combination of these local basis functions.

In the present work, real space is partitioned into tetrahedral elements, and quartic (fourth-order) Lagrange polynomial basis functions are used within each element. The fundamental principles of FEM are summarized in

the Supplementary Material. Once the basis function type and order are fixed, the spatial resolution of the FEM representation depends solely on the mesh density. By refining the mesh into smaller elements, the discretization error can be systematically reduced.

To achieve efficient refinement, FEM naturally supports adaptive mesh refinement (AMR), which concentrates computational effort in regions with the largest estimated errors. In practice, a posteriori error estimators are evaluated for each element, and the mesh is selectively refined in high-error regions—typically near atomic nuclei—thereby enabling accurate all-electron calculations. Further details of the AMR procedure are provided in the Supplementary Material.

In summary, FEM offers several key advantages for molecular all-electron calculations:

1. Adaptive resolution: AMR provides higher spatial resolution near nuclei, ensuring accurate all-electron results.

2. Analytic derivatives: FEM basis functions are analytic polynomials, allowing exact evaluation of derivatives and accurate treatment of the kinetic-energy operator.

3. Computational efficiency: Numerical benchmarks show that for small organic molecules, achieving meV-level convergence of the RPA correlation energy requires only about 300,000 FEM basis functions—an order of magnitude fewer than the 8 million grid points estimated for a comparable finite-difference approach.

Let’s discuss in detail how Eq. 24 is solved within the finite element framework.

To solve this three-dimensional differential equation, we place the target molecule at the center of a cubic region. The selection of the cubic region size (i.e., the approximation to infinity) was discussed in the SM of this work. The cubic region is initially discretized into a set of tetrahedra, followed by several times of uniform refinement to produce the initial mesh. Then, employing the AMR technique, we refine the mesh near atomic nuclei to accurately capture the rapid oscillations of the wavefunctions in these regions. Once a sufficiently dense mesh is generated, the discretization of real space is considered complete.

The next step is to discretize the first-order wavefunction. As we talked before, local basis functions are defined on the degrees of freedom associated with the nodes, edges, and faces of each element. Denoting the set of finite element basis functions as $\{\phi_k\}$, the first-order wavefunction can then be expressed as a linear combination of these basis functions.

$$\psi_i^{(1)}(\mathbf{r}) = \sum_k^{N_f} u_{ik}^{(1)} \phi_k(\mathbf{r}) \quad (4)$$

The ultimate goal of the finite element method is to discretize the differential equations in continuous space into a system of linear equations, and obtain the combination

coefficients of the function to be solved by solving the linear problem. To achieve this, we substitute Eq. 4 into Eq. 24, then left multiply both sides by ϕ'_k and perform integration, resulting in:

$$\sum_k^{N_f} u_{ik}^{(1)} [H_{k'k}^{(0)} - (\epsilon_i - i\omega) S_{k'k}] = \epsilon_i^{(1)} \langle \phi'_k | \psi_i \rangle - V_{k'i}^{(1)} \quad (5)$$

Here, $H_{k'k}^{(0)} = \langle \phi'_k | H^{(0)} | \phi_k \rangle$, $S_{k'k} = \langle \phi'_k | \phi_k \rangle$, $V_{k'i}^{(1)} = \langle \phi'_k | V^{(1)} | \psi_i \rangle$. Eq. 5 essentially represents an expansion of the Sternheimer equation in terms of a general set of functions, which is not restricted to finite element basis functions. However, for finite-element basis functions, due to their highly localized nature, the Hamiltonian and overlap matrices (H and S) are both highly sparse.

Eq. 5 is a linear system of size $N_f \times N_f$. Solving Eq. 5 yields the coefficient vector $\{u_{ik}^{(1)}\}$, which in turn allows us to obtain the first-order wavefunction via Eq. 4. The accuracy of the first-order wavefunction obtained using the finite element method is determined solely by the density of the finite elements. Therefore, by continuously performing adaptive mesh refinement, a converged first-order wavefunction for the system can be achieved. This approach effectively avoids the single-particle basis set error introduced by expanding the first-order wavefunction in a finite basis set.

Solving Eq. 5 on a sufficiently dense finite element mesh can yield first-order wave functions and all-electron RPA correlation energies that are free from basis set incompleteness error. However, in practical calculations, when dealing with molecules containing a larger number of atoms (such as the benzene molecule in this work), a very dense grid may be required, which leads to extremely high computational costs. In the Supplementary Materials, we investigate the convergence of the all-electron RPA correlation energy with respect to finite element mesh density for methane, silane, propyne, and benzene. The results show that for methane, silane and propyne, the correlation energy can be converged to the meV level with approximately 300,000 degrees of freedom under standard Sternheimer method. In contrast, for benzene—a molecule with more atoms—even with around 450,000 degrees of freedom, the accuracy remains limited to about 10 meV.

To enable efficient calculations for larger molecular systems, we developed an improved version of the standard Sternheimer method. This improvement is motivated by the insights gained from our analysis of different basis sets. Atomic orbital (AO) basis sets are highly efficient, using a relatively small number of basis functions to capture most of the Hilbert space, but they lack systematic improvability. Finite element basis sets, on the other hand, offer systematic convergence but are less efficient. If one can combine the strengths of both basis sets, it's possible to overcome their respective limitations. Specifically, if finite element basis functions are used only to

describe the component of the first-order wave function that is not well captured by the AO basis set, the required mesh density can be significantly reduced. The reason is, the AO basis set already provides a good approximation to the first-order wave function, and the residual difference between the exact and AO-approximated first order wavefunctions $\Delta\psi^{(1)}$, is expected to be a smooth and spatially small correction. Representing $\Delta\psi^{(1)}$ in the finite element space is much easier than representing the full first-order wavefunction, since smoother functions require lower spatial resolution.

Thus, by using the finite element basis set solely to represent $\Delta\psi^{(1)}$, we effectively reduce the dependence on a dense finite element mesh. We refer to this framework as the Delta-Sternheimer approach. In the following, we provide a detailed derivation of the working equations for the Delta-Sternheimer approach.

In the following derivation, i represents the occupied states, a represents the unoccupied states, and p represents the general states. First, we define the complete Hilbert space as $\mathcal{H}$. Consider a chosen set of atomic-orbital (AO) basis functions. The AO basis set spans a subspace $\mathcal{H}_{AO}$ of the complete Hilbert space $\mathcal{H}$. The subspace $\mathcal{H}_r$ is defined as the complement of $\mathcal{H}_{AO}$ with respect to $\mathcal{H}$. Solving the ground-state DFT problem in $\mathcal{H}_{AO}$ yields the Kohn–Sham orbitals $\{\psi_{p,AO}\}$ and their energies $\{\epsilon_{p,AO}\}$. We assume that in the complete Hilbert space $\mathcal{H}$, the eigenfunctions and eigenvalues of the DFT Hamiltonian are $\{\psi_p\}$ and $\{\epsilon_p\}$. We can similarly decompose $\mathcal{H}$ and $\mathcal{H}_{AO}$ into occupied subspaces $\mathcal{H}_{occ}$ and $\mathcal{H}_{AO,occ}$, and unoccupied subspaces $\mathcal{H}_{unocc}$ and $\mathcal{H}_{AO,unocc}$, respectively. Here, it should be noted that we assume the chosen AO basis set can provide a complete description of the occupied-state space, i.e., $\mathcal{H}_{AO,occ} = \mathcal{H}_{occ}$. Of course, in practical calculations, a finite atomic orbital basis set also introduces slight errors in the description of the occupied states. But Our tests in the section III of Supplementary Materials demonstrate that the occupied-state manifold obtained in this work affects the RPA correlation energy by less than 1 meV. Therefore, in the following derivations, we do not distinguish between $\mathcal{H}_{occ}$ and $\mathcal{H}_{AO,occ}$, i.e., we no longer differentiate between $\{\psi_i\}$, $\{\epsilon_i\}$ and $\{\psi_{i,AO}\}$, $\{\epsilon_{i,AO}\}$. Therefore, based on this point, $\mathcal{H}_r$ is the complementary subspace of $\mathcal{H}_{AO,unocc}$ with respect to $\mathcal{H}_{unocc}$.

Next, we decompose the first-order wavefunction into contributions from the subspace $\mathcal{H}_{AO}$ $\psi_{i,in}^{(1)}(\mathbf{r}, i\omega)$ and its complementary subspace $\mathcal{H}_r$ $\psi_{i,out}^{(1)}(\mathbf{r}, i\omega)$,

$$\psi_i^{(1)}(\mathbf{r}, i\omega) = \psi_{i,out}^{(1)}(\mathbf{r}, i\omega) + \psi_{i,in}^{(1)}(\mathbf{r}, i\omega) \quad (6)$$

By left-multiplying both sides of Eq. 24 by a unoccupied orbital $\psi_{a,AO}$ in $\mathcal{H}_{AO}$, and integrating over the space, we obtain,

$$\begin{aligned} \langle \psi_{a,AO} | H^{(0)} - \epsilon_i + i\omega | \psi_i^{(1)}(i\omega) \rangle \\ = - \langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle \end{aligned} \quad (7)$$

On the right-hand side of the equation, we use the $\langle \psi_i | \psi_{a,AO} \rangle = 0$ since the i,a represents the occupied states and unoccupied states respectively. Since $\psi_{a,AO}$ is simply the eigenfunction of H_0 in the $\mathcal{H}_{AO}$, we have,

$$H^{(0)}\psi_{a,AO} = \epsilon_{a,AO}\psi_{a,AO} + D_a \quad (8)$$

D_a can be interpreted as the residual function resulting from the diagonalization of $H^{(0)}$ in the finite AO space $\mathcal{H}_{AO}$. D_a lies in the complementary space $\mathcal{H}_r$. For the occupied states, we have,

$$D_i = (H_0 - \epsilon_i)\psi_i = 0. \quad (9)$$

By applying the $H^{(0)}$ to the $\psi_{a,AO}$, we obtain:

$$\begin{aligned} (\epsilon_{a,AO} - \epsilon_i + i\omega) \langle \psi_{a,AO} | \psi_i^{(1)}(i\omega) \rangle \\ + \langle D_a | \psi_i^{(1)}(i\omega) \rangle = - \langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle \end{aligned} \quad (10)$$

define the projection operator P_{AO} ,

$$P_{AO} = \sum_p^{N_{states}} |\psi_{p,AO}\rangle \langle \psi_{p,AO}| \quad (11)$$

Here, N_{states} represents the total number of eigenstates in $\mathcal{H}_{AO}$, including all occupied states and unoccupied states. And we have,

$$\psi_{i,out}^{(1)}(\mathbf{r}, i\omega) = (1 - P_{AO})\psi_i^{(1)}(\mathbf{r}, i\omega) \quad (12)$$

It's very easily to find the relation $\langle D_a | \psi_{i,in}^{(1)}(i\omega) \rangle = 0$ and $\langle \psi_{a,AO} | \psi_{i,out}^{(1)}(i\omega) \rangle = 0$ since the subspaces $\mathcal{H}_{AO}$ and $\mathcal{H}_r$ are orthogonal, substituting Eq. 25 into Eq. 29, we obtain:

$$\langle \psi_{a,AO} | \psi_{i,in}^{(1)}(i\omega) \rangle = \frac{\langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} + \frac{\langle D_a | \psi_{i,out}^{(1)}(i\omega) \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \quad (13)$$

So, one can easily get,

$$\begin{aligned} \psi_{i,in}^{(1)}(\mathbf{r}, i\omega) = \sum_a^{N_{unocc}} \left(\frac{\langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right. \\ \left. + \frac{\langle D_a | \psi_{i,out}^{(1)}(i\omega) \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right) \psi_{a,AO}(\mathbf{r}) \end{aligned} \quad (14)$$

The first term in Eq. 33 corresponds to the sum-over-states expression of the first-order wavefunction. It can

be evaluated by diagonalizing H_0 within the $\mathcal{H}_{AO}$, yielding the eigenfunction set $\{\psi_{p,AO}\}$.

However, the second term reveals something subtle: $\psi_{i,in}^{(1)}$ depends on $\psi_{i,out}^{(1)}$. $\psi_{i,in}^{(1)}$ and $\psi_{i,out}^{(1)}$ are coupled through the residual function D_a , indicating that the origin of this coupling lies in the basis set error introduced by diagonalizing H_0 within the finite $\mathcal{H}_{AO}$. Combine the Eq. 25 and Eq. 33 one can get the expression like,

$$\begin{aligned} \psi_i^{(1)}(\mathbf{r}, i\omega) = \psi_{i,out}^{(1)}(\mathbf{r}, i\omega) \\ + \sum_a^{N_{unocc}} \left(\frac{\langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right. \\ \left. + \frac{\langle D_a | \psi_{i,out}^{(1)}(i\omega) \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right) \psi_{a,AO}(\mathbf{r}) \end{aligned} \quad (15)$$

As shown in Eq. 34, once $\mathcal{H}_{AO}$ is given, the first-order wavefunction in the complete space is fully determined by the component $\psi_{i,out}^{(1)}$ in the $\mathcal{H}_r$ subspace. One can solve the Eq. 5 in the finite element space to obtain $\psi_i^{(1)}$ first, and use the Eq. 31 to obtain $\psi_{i,out}^{(1)}$. As mentioned earlier, ψ_{out} is smoother compared to the full first-order wavefunction, which allows for a significantly reduced finite-element grid density. In the Supplementary Material, we compare the convergence behavior of the standard Sternheimer method and the Delta-Sternheimer method with respect to grid density. It is found that the Delta-Sternheimer method converges faster and more stably with respect to the grid density.

Solving the first-order wave function on a finite-element mesh effectively removes the single-particle basis-set error in RPA correlation energy calculations. However, another source of inaccuracy arises from the completeness error associated with the resolution-of-identity (RI) approximation [51]. But luckily, a systematic comparison of the single-particle and auxiliary basis errors in RI-RPA correlation energies was presented in Ref. [40]. It showed RI error is significantly smaller than the SPBS error. By comparing the atomization energies of diatomic molecules obtained with the RI-Sternheimer approach to the basis-set-error-free reference values reported in Ref.[41], the RI error can be accurately evaluated. Details of the RI error analysis can be found in the SM. The results show that the RI error depends on both the single-particle basis used to generate the auxiliary basis and the maximum angular momentum of the auxiliary functions. When the largest Gaussian basis (aug-cc-pwCV5Z) is used and the auxiliary basis is truncated at angular momentum 9, the RI error can be reduced to the meV-per-atom level.

In our work, we first use FHI-aims [47] to perform all-electron DFT [52] calculations based on the PBE [53] functional. FHI-aims provides us with all the information for ground-state DFT. On the finite-element side, we use

OpenPFEM[54]. This package performs finite-element calculations in a parallel way and internally wraps many PETSc routines, making it easy to solve large sparse linear systems. The specific workflow is as follows. First, the ground-state DFT calculation is performed with FHI-aims. Next, the OpenPFEM package is used to generate the finite-element mesh and carry out adaptive mesh refinement. During this refinement, FHI-aims supplies OpenPFEM with the atomic positions, Kohn–Sham orbitals, eigenvalues, and effective potential. Once the mesh is sufficiently refined, the Sternheimer equation is solved on the dense finite-element grid. From the resulting first-order wavefunctions, the density-response matrix is assembled by integrating over the FEM nodes. Finally, this density-response matrix is returned to FHI-aims to compute the RPA correlation energy. The workflow shows in Fig. 2.

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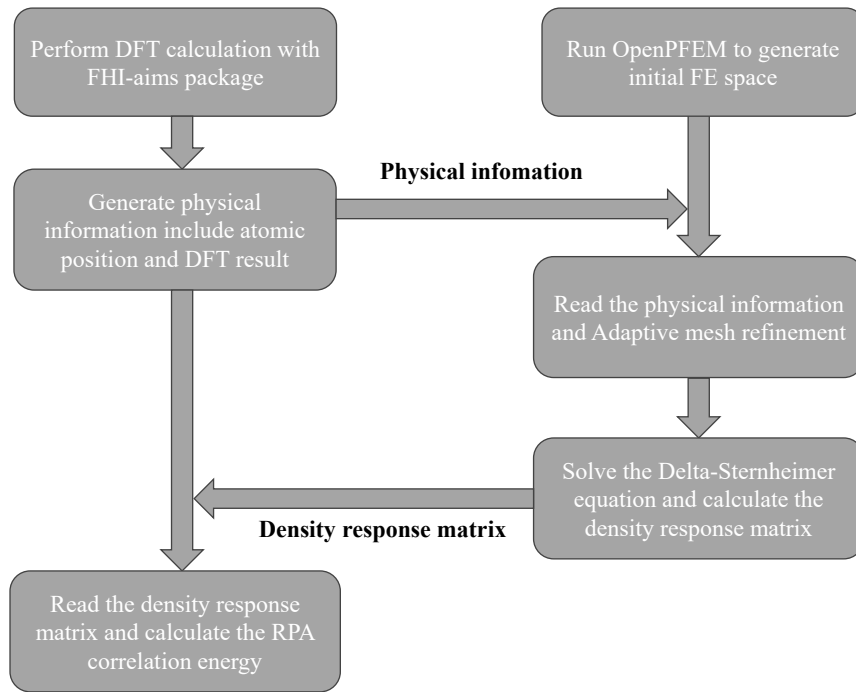


FIG. 2. Workflow.

Supplemental materials for

A finite-element Delta-Sternheimer approach for accurate all-electron RPA correlation energies of arbitrary molecules

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NUMERICAL METHODS

Finite element method

Here, we briefly outline the working principle of the finite element method (FEM). The core of the FEM lies in constructing a finite element (FE) space, and the first step in doing so is to partition the continuous domain. In one-, two-, and three-dimensional spaces, the domain is typically subdivided into line segments, triangles, and tetrahedral elements, respectively. Once the domain has been divided into a collection of elements, local basis functions are defined on each element. These local basis functions are nonzero only on the element itself and a small number of neighboring elements. They are usually chosen to be polynomial functions, with various possible forms and orders. Taking the Laplace boundary-value problem as an example to explain how FEM works, In a bounded domain Ω , the continuous function u satisfies,

$$-\nabla^2 u = f \quad \text{inner of } \Omega \quad (16)$$

$$u = 0 \quad \text{On the boundary } \partial\Omega \quad (17)$$

Suppose we have constructed the FE space V_h , which contains the collection of FE basis functions $\{\varphi_j\}$. In the FE space V_h , we let u_h denote the approximate solution of the partial differential equation 16,

$$u_h = \sum_j^{N_h} u_j \varphi_j \quad (18)$$

Here, N_h is the total number of FE basis. The problem is reduced to solving for the expansion coefficients u_j . By substituting Eq. 18 into Eq. 16, then multiplying on the left by the FE basis function φ_i and integrating over the real space, we obtain,

$$\sum_j^{N_h} a(i, j) u_j = f_i \quad (19)$$

Here, $f_i = \int_{\Omega} f(\mathbf{r}) \varphi_i(\mathbf{r}) d\mathbf{r}$, and $a(i, j)$ represents the,

$$\begin{aligned} a(i, j) &= \int_{\Omega} -\varphi_i(\mathbf{r}) \nabla^2 \varphi_j(\mathbf{r}) d\mathbf{r} \\ &= \int_{\Omega} \nabla \varphi_i(\mathbf{r}) \cdot \nabla \varphi_j(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (20)$$

In the Eq. 20, we apply the integration-by-parts formula and use the fact that the FE basis functions vanish on the boundary. From Eq. 19, we see that in the FE space, the partial differential equation is discretized into a system of linear equations. Moreover, owing to the locality of the FE basis functions, the working matrix (commonly called the stiffness matrix) is sparse. This sparsity provides tremendous advantages for practical computations.

Mesh adaptive refinement

In the FEM, adaptive mesh refinement plays a crucial role in enhancing both computational efficiency and solution accuracy. Because of the complexity of real-world problems, it is often impossible to determine the optimal mesh a priori. Adaptive refinement uses a posteriori error estimates to automatically identify regions requiring finer resolution, thus minimizing computational cost while maintaining accuracy.

The core idea of adaptive refinement is to locally enrich the mesh in areas where the estimated error is large, while keeping a coarser mesh in regions where the error is small. This strategy not only effectively improves accuracy, but also avoids the dramatic increase in computational workload associated with global refinement. By iterating the adaptive refinement process several times, the mesh distribution can be progressively optimized, concentrating computational effort precisely where it is most needed.

In the adaptive refinement process, a posteriori error estimator is used to generate an error indicator for each mesh element. For the boundary-value problem Eq. 16, the K -th element error indicator η_K is defined as follows,

$$\eta_K^2(u_h, f) = h_K^2 \|f + \nabla^2 u_h\|_{0,K}^2 + \sum_{e \in \mathcal{E}_K} h_e \left\| \left[\frac{\partial u_h}{\partial \mathbf{n}} \right] \right\|_{0,e}^2, \quad (21)$$

Here, h_K denotes the diameter of element K , and h_e denotes the diameter of a face (3 dimensional) or an edge (2 dimensional) of element K . The quantity $\frac{\partial u_h}{\partial \mathbf{n}}$ represents the derivative of the FE solution u_h in the outward normal direction on the face (3 dimensional) or edge (2 dimensional) e . $\mathcal{E}_K$ denotes the set of all faces (3 dimensional) or edges (2 dimensional) of element K .

Accordingly, the global a posteriori error estimate can be defined as follows,

$$\eta_h^2(u_h, f) = \sum_{K \in \mathcal{T}_h} \eta_K^2(u_h, f) \quad (22)$$

$\mathcal{T}_h$ denotes the FE mesh.

We adopt the Dörfler marking strategy to select the elements requiring local refinement based on the error indicator Eq. 21[55],

(1). Sorting: Arrange all elements in descending order of their error indicators, i.e. $\eta_{K_1} \geq \eta_{K_2} \geq \dots \geq \eta_{K_N}$.

(2). Accumulation Selection: choose the smallest number of elements M (i.e. the first M in the sorted list), such that their cumulative error exceeds a given threshold $\theta \in (0, 1)$,

$$\sum_i^M \eta_{K_i}^2 \geq \theta \eta_h^2(u_h, f) \quad (23)$$

Delta-Sternheimer Framework

Here, we derive the Delta-Sternheimer framework based on the standard Sternheimer equation, Eq. 24.

$$(H^{(0)} - \epsilon_i + i\omega) \psi_i^{(1)}(\mathbf{r}, i\omega) = (\epsilon_i^{(1)} - V^{(1)}) \psi_i(\mathbf{r}) \quad (24)$$

First, we define the complete Hilbert space as $\mathcal{H}$. Consider a chosen set of atomic-orbital (AO) basis functions. The AO basis set spans a subspace $\mathcal{H}_{AO}$ of the complete Hilbert space $\mathcal{H}$. The subspace $\mathcal{H}_r$ is defined as the complement of $\mathcal{H}_{AO}$ with respect to $\mathcal{H}$. Solving the ground-state DFT problem in $\mathcal{H}_{AO}$ yields the Kohn-Sham orbitals $\{\psi_{p,AO}\}$ and their energies $\{\epsilon_{p,AO}\}$. We assume that in the complete Hilbert space $\mathcal{H}$, the eigenfunctions and eigenvalues of the DFT Hamiltonian are $\{\psi_p\}$ and $\{\epsilon_p\}$. We can similarly decompose $\mathcal{H}$ and $\mathcal{H}_{AO}$ into occupied subspaces $\mathcal{H}_{occ}$ and $\mathcal{H}_{AO,occ}$, and unoccupied subspaces $\mathcal{H}_{unocc}$ and $\mathcal{H}_{AO,unocc}$, respectively. Here, it should be noted that we assume the chosen AO basis set can provide a complete description of the occupied-state space, i.e., $\mathcal{H}_{AO,occ} = \mathcal{H}_{occ}$. Of course, in practical calculations, a finite atomic orbital basis set also introduces slight errors in the description of the occupied states. But Our tests in the section III of Supplementary Materials demonstrate that the occupied-state manifold obtained in this work affects the RPA correlation energy by less than 1 meV. Therefore, in the following derivations, we do not distinguish between $\mathcal{H}_{occ}$ and $\mathcal{H}_{AO,occ}$, i.e., we no longer differentiate between $\{\psi_i\}$, $\{\epsilon_i\}$ and $\{\psi_{i,AO}\}$, $\{\epsilon_{i,AO}\}$. Therefore, based on this point, $\mathcal{H}_r$ is the complementary subspace of $\mathcal{H}_{AO,unocc}$ with respect to $\mathcal{H}_{unocc}$.

Next, we decompose the first-order wavefunction into contributions from the subspace $\mathcal{H}_{AO}$ $\psi_{i,in}^{(1)}(\mathbf{r}, i\omega)$ and its

complementary subspace $\mathcal{H}_r$ $\psi_{i,out}^{(1)}(\mathbf{r}, i\omega)$,

$$\psi_i^{(1)}(\mathbf{r}, i\omega) = \psi_{i,out}^{(1)}(\mathbf{r}, i\omega) + \psi_{i,in}^{(1)}(\mathbf{r}, i\omega) \quad (25)$$

By left-multiplying both sides of Eq. 24 by a unoccupied orbital $\psi_{a,AO}$ in $\mathcal{H}_{AO}$, and integrating over the space, we obtain,

$$\begin{aligned} \langle \psi_{a,AO} | H^{(0)} - \epsilon_i + i\omega | \psi_i^{(1)}(i\omega) \rangle \\ = - \langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle \end{aligned} \quad (26)$$

On the right-hand side of the equation, we use the $\langle \psi_i | \psi_{a,AO} \rangle = 0$ since the i , a represents the occupied states and unoccupied states respectively. Since $\psi_{a,AO}$ is simply the eigenfunction of H_0 in the $\mathcal{H}_{AO}$, we have,

$$H^{(0)} \psi_{a,AO} = \epsilon_{a,AO} \psi_{a,AO} + D_a \quad (27)$$

D_a can be interpreted as the residual function resulting from the diagonalization of $H^{(0)}$ in the finite AO space $\mathcal{H}_{AO}$. D_a lies in the complementary space $\mathcal{H}_r$. For the occupied states, we have,

$$D_i = (H_0 - \epsilon_i) \psi_i = 0. \quad (28)$$

By applying the $H^{(0)}$ to the $\psi_{a,AO}$, we obtain:

$$\begin{aligned} (\epsilon_{a,AO} - \epsilon_i + i\omega) \langle \psi_{a,AO} | \psi_i^{(1)}(i\omega) \rangle \\ + \langle D_a | \psi_i^{(1)}(i\omega) \rangle = - \langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle \end{aligned} \quad (29)$$

define the projection operator P_{AO} ,

$$P_{AO} = \sum_p^{N_{states}} |\psi_{p,AO}\rangle \langle \psi_{p,AO}| \quad (30)$$

Here, N_{states} represents the total number of eigenstates in $\mathcal{H}_{AO}$, including all occupied states and unoccupied states. And we have,

$$\psi_{i,out}^{(1)}(\mathbf{r}, i\omega) = (1 - P_{AO}) \psi_i^{(1)}(\mathbf{r}, i\omega) \quad (31)$$

It's very easily to find the relation $\langle D_a | \psi_{i,in}^{(1)}(i\omega) \rangle = 0$ and $\langle \psi_{a,AO} | \psi_{i,out}^{(1)}(i\omega) \rangle = 0$ since the subspaces $\mathcal{H}_{AO}$ and $\mathcal{H}_r$ are orthogonal, substituting Eq. 25 into Eq. 29, we obtain:

$$\langle \psi_{a,AO} | \psi_{i,in}^{(1)}(i\omega) \rangle = \frac{\langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} + \frac{\langle D_a | \psi_{i,out}^{(1)}(i\omega) \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \quad (32)$$

So, one can easily get,

$$\begin{aligned} \psi_{i,in}^{(1)}(\mathbf{r}, i\omega) = \sum_a^{N_{unocc}} \left(\frac{\langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right. \\ \left. + \frac{\langle D_a | \psi_{i,out}^{(1)}(i\omega) \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right) \psi_{a,AO}(\mathbf{r}) \end{aligned} \quad (33)$$

The first term in Eq. 33 corresponds to the sum-over-states(SOS) expression of the first-order wavefunction. It can be evaluated by diagonalizing H_0 within the $\mathcal{H}_{AO}$, yielding the eigenfunction set $\{\psi_{p,AO}\}$.

However, the second term reveals something subtle: $\psi_{i,in}^{(1)}$ depends on $\psi_{i,out}^{(1)}$. $\psi_{i,in}^{(1)}$ and $\psi_{i,out}^{(1)}$ are coupled through the residual function D_a , indicating that the origin of this coupling lies in the basis set error introduced by diagonalizing H_0 within the finite $\mathcal{H}_{AO}$. Combine the Eq. 25 and Eq. 33 one can get the expression like,

$$\begin{aligned} \psi_i^{(1)}(\mathbf{r}, i\omega) = & \psi_{i,out}^{(1)}(\mathbf{r}, i\omega) \\ & + \sum_a^{N_{unocc}} \left(\frac{\langle \psi_{a,AO} | V^{(1)} | \psi_i \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right. \\ & \left. + \frac{\langle D_a | \psi_{i,out}^{(1)}(i\omega) \rangle}{\epsilon_i - \epsilon_{a,AO} - i\omega} \right) \psi_{a,AO}(\mathbf{r}) \quad (34) \end{aligned}$$

As shown in Eq. 34, once $\mathcal{H}_{AO}$ is given, the first-order wavefunction in the complete space is fully determined by the component $\psi_{i,out}^{(1)}$ in the $\mathcal{H}_r$ subspace. One can solve the Eq(5) of the main text in the FE space to obtain $\psi_i^{(1)}$ first, and use the Eq. 31 to obtain $\psi_{i,out}^{(1)}$. As mentioned earlier, ψ_{out} is smoother compared to the full first-order wavefunction, which allows for a significantly reduced FE grid density.

IMPLEMENTATION DETAILS

In our work, we first use FHI-aims [47] to perform all-electron(AE) DFT [52] calculations based on the PBE [53] functional. FHI-aims provides us with all the information for ground-state DFT. On the FE side, we use OpenPFEM[54]. This package performs FE calculations in a parallel way and internally wraps PETSC routines [56], making it easy to solve large sparse linear systems. The specific workflow is as follows. First, the ground-state DFT calculation is performed with FHI-aims. Next, the OpenPFEM package is used to generate the FE mesh and carry out adaptive mesh refinement. During this refinement, FHI-aims supplies OpenPFEM with the atomic positions, Kohn–Sham orbitals, eigenvalues, and effective potential. Once the mesh is sufficiently refined, the Sternheimer equation is solved on the dense FE grid. From the resulting first-order wavefunctions, the density-response matrix is assembled by integrating over the FE space. Finally, this density-response matrix is returned to FHI-aims to compute the RPA correlation energy.

Obtaining adaptive mesh

In the Sec. I.B, we discuss the adaptive mesh refinement approach for FE mesh based on posteriori error. It should be noted that the posteriori error estimator is defined with respect to a particular differential equation. In our work, for a given molecular configuration, we need to solve the Sternheimer equation for different occupied-state orbitals, different spatial distributions of the perturbation, and different frequency points. If we perform adaptive refinement separately for each of these equations, we would obtain extremely similar meshes, resulting in a substantial waste of computational resources.

Here, we choose instead to solve the Sternheimer equation for all occupied states in the static case ($\omega = 0$) under a single representative perturbation. We then define the total posteriori error on each element as the sum of the local error estimators for each occupied-state orbital. In this way, we generate one FE mesh tailored to the molecule. The choice of representative perturbation is also very simple and intuitive. we choose,

$$V^{(1)}(\mathbf{r}) = \alpha \mathbf{V}_{\text{ext}}(\mathbf{r}) \quad (35)$$

we set $\alpha=0.1$, such a choice is physically well motivated, since the external potential naturally encodes the positions and atomic numbers of the constituent atoms. The corresponding FE mesh generated from this perturbation exhibits a desirable feature: it is refined in the vicinity of atomic nuclei and becomes gradually coarser in regions farther away.

CONVERGENCE TEST

In our approach, the accuracy of the RPA correlation energy calculation mainly depends on the following two aspects: (1) the mesh density of the FE, (2) the resolution of identity (RI) error, i.e., the completeness of the auxiliary basis set. We will discuss these two aspects in the subsections and separately below. As for other parameters affecting the calculations, such as the choice of the asymptotic size (i.e., the size of the cubic box) and the errors introduced by using LCAO occupied states, the convergence of these parameters will be discussed together in subsection C. In subsections D and E, we compare our calculated results with Ref. [41] and Ref. [30], respectively, as benchmark references to check the reliability of our calculations.

Converge behavior with respect to the mesh density for the standard Sternheimer method and the Delta-Sternheimer method.

Here, we tested methane, silane, propyne, and benzene to examine the convergence of their RPA correla-

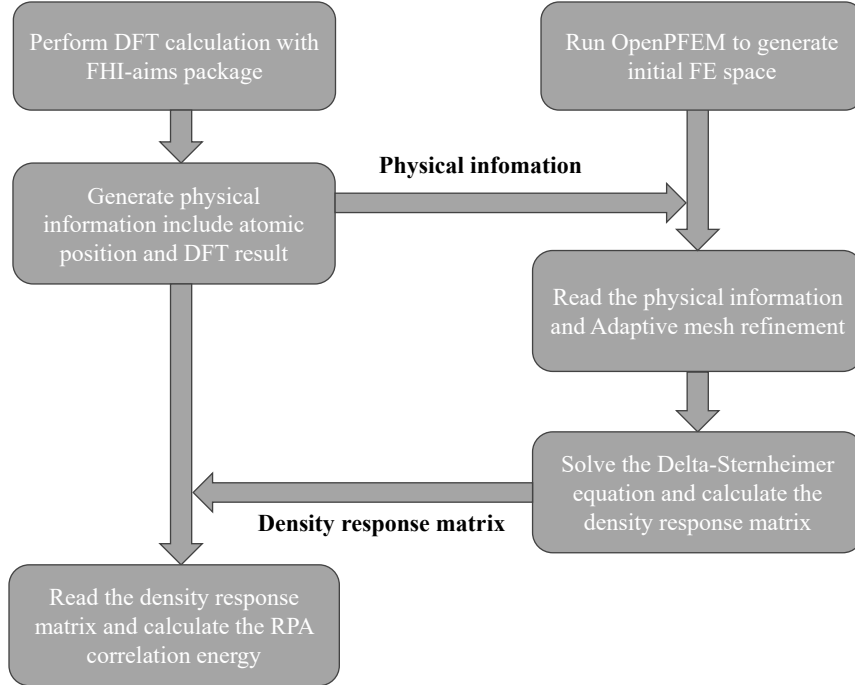
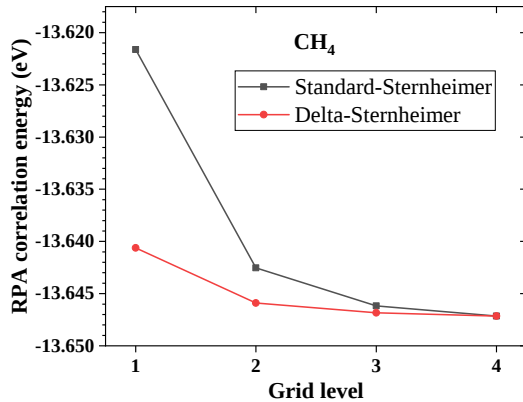


FIG. 3. Workflow.

tion energies with respect to grid density under Standard-Sternheimer method and Delta-Sternheimer method, respectively. The computational parameters here are as follows: DFT calculations are performed using the aug-cc-pwCV5Z basis set, and the auxiliary basis set is generated on-the-fly. 32 Gaussian-Legendre grid points are used. The size of the finite element box is 40 bohr. Taking methane as an example, the results are shown in Fig. 4,

FIG. 4. Converge behavior with respect to the mesh density of CH₄.

It can be readily seen that, at the same grid density, the Delta-Sternheimer method yields lower correlation ener-

gies and converges much faster with respect to grid refinement. We also observe that when the grid is relatively coarse—for example, at Grid level = 1, the energy difference between the two methods is rather large – about 20 meV. This can be understood as the finite AO space used in the Delta-Sternheimer method providing an effective compensation to the incomplete finite-element space. At Grid level = 4, the correlation energies obtained by the standard Sternheimer and Delta-Sternheimer methods differ by only 0.02 meV, which indicates that the finite-element space is already very close to completeness and that the finite AO space in the Delta-Sternheimer method is almost fully contained in the finite-element space. As a result, the two methods yield essentially identical results.

In Tab. III, we report the number of degrees of freedom (NOF, i.e., the total number of basis functions in the finite-element space) for each grid level in Fig. 4, along with the RPA correlation energies obtained from both methods. Results for other molecules are also presented. It can be seen that the results for silane are similar to those for methane. For propyne, however, the Standard-Sternheimer method shows a certain degree of numerical instability: at Grid levels 2, 3, and 4, the RPA correlation energies fluctuate on the meV scale. The case of benzene, the largest molecule studied in this work, is of particular importance. First, we find that for the Standard-Sternheimer method, even with as many as 450,000 grid degrees of freedom, the correlation energy converges only to the 10 meV level and exhibits relatively large numer-

ical fluctuations. This demonstrates that for molecules with a larger number of atoms, the computational cost of using the Standard-Sternheimer method becomes extremely high. In contrast, the Delta-Sternheimer method already reaches meV-level convergence at Grid level = 3. We further note that, for benzene, the RPA correlation energy obtained by the Delta-Sternheimer method does not decrease monotonically but instead converges upward from a lower value, which differs from the results for the three smaller molecules. Moreover, at Grid levels 3, 4, 5, and 6, small numerical oscillations below 1 meV are observed. These instabilities may originate from inherent issues associated with higher-order finite-element basis functions. Nevertheless, in the Delta-Sternheimer method, this phenomenon appears only for the relatively large benzene molecule, and the magnitude of the oscillations remains extremely small. Therefore, it does not affect the conclusion that the Delta-Sternheimer method can significantly accelerate the convergence of the RPA correlation energy with respect to the finite-element grid density and provides better numerical stability. Another important conclusion is that, for benzene, the largest molecule studied in this work, the RPA correlation energy obtained with the Delta-Sternheimer method converges to the meV level at a grid density corresponding to about 300,000 degrees of freedom. Consequently, for all of the several dozen small molecules investigated in this work, the finite element grid degrees of freedom were adaptively refined to at least 300,000.

RI-error Test

In Section III.A, we tested the convergence of the RPA correlation energy with respect to the finite-element grid. The results show that when the NOF reaches approximately 300,000, the RPA correlation energy can be converged to the meV level. Consequently, in the RPA calculations, the SPBS error which represents the most significant part of the basis-set error, has been almost completely eliminated (the SPBS error associated with the description of the occupied-state manifold will be discussed in the next section). However, within the RI framework one must also ensure the completeness of the ABS. Although Ref. [40] shows that the incompleteness error of the ABS is much smaller than that of the SPBS, it's still visible in practical computations. In Ref. [40] and Ref. [41], we completely eliminated the RI approximation by employing iterative diagonalization to obtain basis-error-free results. While iterative diagonalization could likewise eliminate RI errors here, it is prohibitively expensive. For the mono- and diatomic systems treated in Ref. [40] and Ref. [41], full convergence of the correlation energy is achievable, but it becomes exceedingly difficult for the general molecules considered in this work. Accordingly, we compute RPA correlation energies within

the RI framework in this work and perform extensive tests to quantify the RI error.

Here we examine the RI-RPA atomization energies of a series of diatomic molecules in the prolate spheroidal coordinate system of Ref. [41], and compare them to the basis-error-free results reported in Ref. [41], thereby estimating the RI incompleteness error in atomization energy level. It should be noted that, since solving the Sternheimer equation in prolate spherical coordinates eliminates single-particle basis-set errors, the differences in atomization energies obtained via the RI approach compared to the reference values of Ref. [41] arise entirely from the auxiliary basis sets. Therefore, these differences can be taken as a measure of the auxiliary basis-set error. The tests include comparisons of errors from (i) auxiliary basis sets generated on-the-fly from single-particle basis sets versus those from optimal RI-fitting auxiliary basis sets, (ii) auxiliary basis sets generated on-the-fly from different type of correlation-consistent basis set, and (iii) auxiliary basis sets with varying maximum angular momentum. We tested the effects of auxiliary basis sets generated on-the-fly using the aug-cc-pwCV5Z and NAO-VCC-5Z basis sets on the atomization energies of a series of diatomic molecules. Two cases for the maximum angular momentum of the auxiliary basis functions, 5 and 9, were considered. In addition, we tested the pre-optimized auxiliary basis set aug-cc-pwCV5Z-RI-FITTING. The results are presented in Tables Tab. V, while Tab. IV lists the sizes of the different auxiliary basis sets used in this test, for the purpose of evaluating computational efficiency.

It can be seen that the auxiliary basis set generated on-the-fly using aug-cc-pwCV5Z yields the smallest error. When the maximum angular momentum is set to 9, the results deviate from the reference by only 0.04 kcal/mol. The cost, however, is 1,000–2,000 auxiliary basis functions per atom. We also note that increasing the maximum angular momentum of the auxiliary basis set is an effective way to reduce the auxiliary-basis error, although this also leads to a significant increase in the basis-set size. Another point worth mentioning is the efficiency of the pre-optimized auxiliary basis set. With only 300–400 auxiliary basis functions per atom, the RI error can be reduced to 0.28 kcal/mol, corresponding to approximately 10 meV. Therefore, different auxiliary basis sets can be chosen depending on the desired computational accuracy. In this work, solving the Delta-Sternheimer equation within the finite element framework allows us to almost completely eliminate the single-particle basis set error (see Sec. III A). To further minimize the RI error, we employ the aug-cc-pwCV5Z basis set and set the maximum angular momentum of the auxiliary basis functions to 9 when we calculate the atomization energy of molecules.

Molecule	Grid Level	NOF	S-S	D-S
CH ₄	1	94159	-13.62162	-13.64063
	2	12374	-13.64253	-13.64591
	3	18206	-13.64618	-13.64683
	4	238577	-13.64714	-13.64716
SiH ₄	1	115407	-26.59912	-26.61804
	2	160219	-26.62194	-26.62600
	3	200047	-26.62709	-26.62719
	4	242887	-26.62764	-26.62749
C ₃ H ₄	1	142178	-32.64365	-32.72890
	2	194536	-32.73711	-32.73562
	3	248803	-32.73611	-32.73708
	4	301035	-32.73873	-32.73748
C ₆ H ₆	1	214459	-60.33976	-60.62535
	2	250419	-60.36203	-60.62368
	3	316203	-60.48645	-60.60552
	4	360963	-60.55359	-60.60496
	5	405935	-60.60568	-60.60529
	6	458385	-60.60065	-60.60554

TABLE III. RPA correlation energy convergence with respect to FE mesh density for CH₄, SiH₄, C₃H₄, and C₆H₆. The energy unit is eV. S-S represents the FE Standard-Sternheimer approach, and D-S represents the FE Delta-Sternheimer approach.

ATOM	OPT	aug-cc-pwCV5Z		NAO-VCC-5Z	
		$L_{\max} = 5$	$L_{\max} = 9$	$L_{\max} = 5$	$L_{\max} = 9$
H	189	412	863	224	310
C	323	669	1311	362	589
N	323	664	1306	366	593
O	324	675	1332	352	579
F	324	665	1322	374	629
P	411	875	1805	484	769
Cl	411	879	1796	505	807

TABLE IV. Basis-set size of different ABS for different elements.

TABLE V. RI-RPA atomization energy for several diatomic molecules. OTF-Gaussian denotes the auxiliary basis generated on-the-fly with the aug-cc-pwCV5Z basis set, while OTF-NAO denotes the auxiliary basis generated on-the-fly with the NAO-VCC-5Z basis set. $L_{\max}$ represents the maximum angular momentum of the OTF auxiliary basis. OPT refers to the pre-optimized auxiliary basis aug-cc-pwCV5Z-RIFIT. Δ indicates the deviation from the reference, with the reference taken from Ref. [41]. The energy unit is kcal/mol.

MO	OTF-Gaussian				OTF-NAO				OPT		Reference
	$L_{\max}=5$	$L_{\max}=9$	$\Delta(5)$	$\Delta(9)$	$L_{\max}=5$	$L_{\max}=9$	$\Delta(5)$	$\Delta(9)$	RI	Δ	
N ₂	-224.16	-224.36	0.24	0.04	-223.91	-224.14	0.49	0.26	-223.97	0.43	-224.40
O ₂	-113.65	-113.68	0.14	0.11	-113.37	-113.48	0.42	0.31	-113.49	0.30	-113.79
P ₂	-116.80	-117.14	0.39	0.05	-116.63	-117.16	0.56	0.03	-116.65	0.54	-117.19
CO	-245.48	-245.56	0.13	0.06	-245.36	-245.51	0.25	0.10	-245.27	0.34	-245.61
H ₂	-108.73	-108.74	-0.01	-0.02	-108.71	-108.71	0.01	0.01	-108.68	0.04	-108.72
Cl ₂	-50.11	-50.18	0.07	0.00	-49.54	-49.79	0.64	0.39	-49.86	0.32	-50.18
HF	-132.93	-132.76	-0.16	0.01	-132.88	-132.78	-0.11	-0.01	-132.66	0.11	-132.77
F ₂	-30.54	-30.61	0.07	0.00	-30.31	-30.44	0.30	0.17	-30.48	0.13	-30.61
MAE	—	—	0.16	0.04	—	—	0.35	0.16	—	0.28	—

Converge behavior with respect to cubic box size and basis set for describing the occupied manifold

In this section, we first examine the effect of the choice of the simulation box on the calculations. The box size determines the placement of the molecule: if the box is too small, the wavefunction does not decay to zero at the boundaries; if the box is too large, computational resources are wasted. Therefore, we first tested the RPA correlation energy of the acetylene molecule using different box sizes. The basis set employed was aug-cc-pwCV5Z, and the pre-optimized auxiliary basis set aug-cc-pwCV5Z-RI-FITTING was used. Box sizes of 30, 40, and 50 bohr were considered. All other parameters were kept the same, and the resulting RPA correlation energies are summarized as follows:

TABLE VI. Convergence test of RPA correlation energy with respect to box size. The energy unit is eV.

Molecule	30	40	50
C ₂ H ₂	-20.91153	-20.91151	-20.91149
PH ₃	-27.61443	-27.61470	-27.61479

From Tab. VI it can be seen that, as the size of the cubic box increases from 30 bohr to 50 bohr, the change in the correlation energy is less than 0.1 meV. This indicates that in the present calculations the box size does not need to be particularly large. It should be noted that in Ref. [41] we also discussed the effect of the choice of infinity in prolate spheroidal coordinates on the correlation energy. In Ref. [41], we found that setting infinity at 40 bohr still leads to an absolute correlation energy error of several meV. In contrast, the convergence with respect to infinity in the present work is much faster. The difference arises from the fact that the present calculations are performed at the RI-RPA level. In our approach, the auxiliary basis functions localized within a few bohr around the atomic centers are regarded as perturbations to the system, and the resulting first-order density is subsequently projected back onto the auxiliary basis functions. Therefore, the computational framework employed here is insensitive to the choice of infinity.

Next, we examine the completeness of the occupied-state manifold described by atomic orbitals. In this work, only the occupied states obtained from atomic orbital basis-set calculations are required. Basis set affects two parts of total RPA energy specifically: (1) the RPA correlation energy, where the occupied-state energies and wavefunctions used in solving the Sternheimer equation in the finite-element space depend on the chosen basis set; and (2) the non-self-consistent Hartree-Fock energy, where the single particle energies, hartree energies and exact change energies are only depended on the occupied manifold. In this work, we primarily employ the aug-cc-pwCV5Z basis set, as we have tested its accuracy in terms of both the RPA correlation energy and the non-

self-consistent HF energy.

To examine the convergence of the RPA correlation energy with respect to the single-particle basis set describing the occupied-state manifold, we performed calculations starting from aug-cc-pwCVTZ, aug-cc-pwCVQZ, and aug-cc-pwCV5Z, and analyzed the dependence of the RPA correlation energy on the basis set. To eliminate the influence of the auxiliary basis, the same pre-optimized aug-cc-pwCV5Z-RI-FITTING auxiliary basis set was used for all single-particle basis sets. The box size was set to 30 bohr, and identical finite-element grids were used for all calculations, with 32 Gauss-Legendre frequency points. The results are summarized in Tab. VII. It can be observed that the difference between the QZ and 5Z calculations is less than 1 meV. Even when using only the TZ basis for the DFT calculation, the impact on the RPA correlation energy is merely 1–2 meV. Therefore, the RPA correlation energy converges rapidly with respect to the atomic orbital basis set describing the occupied-state manifold.

With respect to the basis set convergence of the non-self-consistent Hartree-Fock energy, detailed tests are provided in Table X in the following section. The results demonstrate that, at the level of atomization energies, the non-self-consistent HF contribution obtained with the aug-cc-pwCV5Z basis set converges to the meV level.

TABLE VII. Converge behavior with respect to the basis set used for describing the occupied manifold. The energy unit is eV.

Molecule	TZ	QZ	5Z
C ₂ H ₂	-20.90956	-20.91073	-20.91153
PH ₃	-27.61540	-27.61416	-27.61443
C ₃ H ₆	-34.64236	-34.64270	-34.64356
H ₂ O	-15.76272	-15.76281	-15.76321

Benchmark with Sternheimer method in prolate spherical coordinate system

In this section, we compare the RI-RPA correlation energies obtained in the finite-element (FE) space and in the prolate-spheroidal coordinate system under identical conditions, as one of the benchmark tests of this work. Specifically, we tested the N₂ molecule, using aug-cc-pwCV5Z for the DFT calculations, with the auxiliary basis generated on-the-fly. The frequency integration employed 32 Gauss-Legendre grid points. For the prolate-spheroidal coordinate system, the computational parameters were set to N_μ = 192 and N_ν = 150, which ensures that the correlation energy is converged to the sub-meV level; this result is therefore taken as the reference for the FE calculations. For the FE space, similar to Section A, we computed the RPA correlation energy using both the Standard-Sternheimer and Delta-Sternheimer

approaches with progressively refined FE grids, in order to examine whether the FE method can converge to the vicinity of the reference value. The results are as follows in Tab. VIII. From Tab. VIII, it can be seen that for the

Grid level	NOF	S-S	D-S
1	114139	-23.10559(106.85)	-23.19675(15.69)
2	142195	-23.21279(-0.35)	-23.21094(1.50)
3	178491	-23.21273(-0.29)	-23.21149(0.95)
4	233917	-23.21168(0.76)	-23.21196(0.48)

TABLE VIII. Benchmark with prolate spherical coordinate system. Reference value: -23.21244 eV. The unit in table is eV. The values in parentheses denote the deviations from the reference results, in units of meV. S-S represents the FE Standard-Sternheimer approach, and D-S represents the FE Delta-Sternheimer approach.

present test, the Delta-Sternheimer method converges to the meV level already at grid level 3. At grid level 4, the result obtained by Delta-Sternheimer differs from the reference by only 0.48 meV. For the Standard-Sternheimer method, a slight numerical instability is observed, as already discussed in Section A. Nevertheless, at grid level 4, the Standard-Sternheimer result also deviates from the reference by only 0.76 meV.

Benchmark with F12 result

Humer et al systematically investigated the basis-set convergence of the direct RPA (dRPA) correlation energy by combining plane-wave projector augmented-wave (PAW) calculations with explicitly correlated Gaussian-type orbital (dRPA-F12) methods[30]. In the GTO part, the introduction of the F12 approach accelerates the basis-set convergence of the RPA correlation energy, thereby yielding results close to the basis-set limit. In Ref. [41], we have already verified the reliability of the F12 results at the level of diatomic molecules. Therefore, in the present work, we also compare with that study as another benchmark.

As shown in Tab. IX, the mean absolute error of the atomization energies obtained from both the F12 method and the present work is 0.13 kcal/mol (for both AE and frozen core(FC) cases). This demonstrates that the F12 method can effectively eliminate basis set errors and also confirms the accuracy of the results obtained in this work.

RESULT

The main significance of the present work lies in correcting the single-particle basis-set errors that commonly affect RPA calculations for small molecules. We are therefore particularly interested in how finite single-particle basis sets influence energy differences under

RPA. In the Results section, we present tests in two aspects. In the first part, we examine the small energy differences between different configurations of the water dimer. We compare results obtained using the finite-basis SOS method with those obtained in this work using the finite-element Delta-Sternheimer approach. By testing three widely used correlation-consistent basis sets, we assess the impact of finite single-particle basis-set errors on the calculation of energy differences in the water dimer.

In the second part, we select 50 small molecules containing elements from the first three periods from the G-97 set and compute their RPA atomization energies. These results are compared with those obtained using the finite-basis SOS approach to evaluate the errors arising from finite basis sets in RPA atomization energy calculations. At the same time, we also compute results extrapolated from correlation-consistent basis sets and, by comparison with our finite-element results, assess the errors and reliability of the extrapolation approach.

Basis-set-issue check for water dimer

We first apply this technique to the calculation of the water dimer. The energy differences between various configurations of the water dimer are extremely small. Our primary interest lies in evaluating how accurately these energy differences can be described using different types and sizes of atomic orbital (AO) basis sets—that is, whether the basis set incompleteness error is significant. To this end, we randomly selected 20 configurations from a 200-step molecular dynamics trajectory of the water dimer. For each of these 20 geometries, we performed adaptive mesh refinement in the finite-element space to compute their RPA correlation energies, which are taken as reference values for the RPA correlation energy. The single-particle basis sets used are the tier basis sets provided by FHI-AIMS, which have been shown to yield highly converged DFT results. Therefore, we also take the 1 Hartree-Fock(HF) energy (i.e., the sum of kinetic energy, Hartree energy, and exact exchange energy) calculated using this basis set as the reference for the HF part. The results to be compared are obtained using the SOS approach with different types of correlation-consistent basis sets. Our goal is to assess whether the energy differences between different water dimer configurations predicted by these basis sets are reliable. In this work, we tested three types of correlation-consistent basis sets: (1) aug-cc-pwCVXz, (2) cc-pVXz, and (3) NAO-VCC-nZ. Another important point to note is that all calculations in this part were performed using the same auxiliary basis sets. Specifically, we employed the largest RI-fitting basis sets available from the Basis Set Exchange website: aug-cc-pwCV5Z-RIFIT for oxygen and aug-cc-pV6Z-RIFIT for hydrogen. The choice of identical auxiliary basis sets across all calculations was

MO	F12 AE	This work AE	$\Delta(\text{AE})$	F12 FC	This work FC	$\Delta(\text{FC})$
HCN	-300.70	-300.54	-0.16	-298.87	-298.69	-0.18
H ₂ O	-223.60	-223.57	-0.04	-223.19	-223.26	0.07
H ₂ O ₂	-256.34	-256.30	-0.04	-255.81	-255.78	-0.03
CH ₄	-405.94	-406.10	0.16	-494.77	-494.93	0.16
C ₂ H ₆	-685.92	-686.11	0.19	-683.68	-683.89	0.21
C ₂ H ₂	-383.62	-383.47	-0.15	-381.17	-381.02	-0.15
C ₂ H ₄	-539.60	-539.70	0.10	-537.30	-537.41	0.11
CO ₂	-366.85	-366.44	-0.41	-364.76	-364.51	-0.25
CH ₄ O	-492.23	-492.28	0.05	-490.83	-490.92	0.09
CH ₂ O	-357.08	-356.97	-0.11	-355.69	-355.62	-0.07
NH ₃	-291.25	-291.30	0.05	-290.55	-290.65	0.10
N ₂ H ₄	-427.82	-427.91	0.09	-426.63	-426.72	0.09
MAE	/	/	0.13	/	/	0.13

TABLE IX. Comparison between F12 and this-work results (AE/FC). The energy unit is kcal/mol, rounded to two decimals.

intentional, as our primary focus is on the error introduced by the single-particle basis sets, not the resolution-of-identity (RI) approximation. Furthermore, the use of the largest available RI-fitting basis sets ensures that the RI error remains negligible. We sorted the 20 water dimer configurations in ascending order of total energy. The configuration with the lowest energy was taken as the reference, and the energy differences of the other configurations were calculated relative to this reference. We then compared the energy differences obtained with different correlation-consistent basis sets to those obtained using the Delta-Sternheimer method. The results are shown in the figure below. It is clear that as the basis set size increases, the energy difference curves obtained from the three different types of correlation-consistent basis sets gradually approach the reference results from the Delta-Sternheimer method. To quantify the basis set error, we calculate,

$$Error = \sum_{j=2}^{20} \frac{|\Delta_j - \Delta_j^{REF}|}{19} \quad (36)$$

Here, $\Delta_j = E_j - E_1$, E_j and E_1 represent the energy of j -th configuration and the lowest-energy configuration. The superscript "REF" denotes the energy obtained from the Delta-Sternheimer method, while values without a superscript correspond to the energies calculated using different correlation-consistent basis sets. We can separately calculate the basis set errors for the total energy, the HF total energy, and the RPA correlation energy. The results are shown below (energy unit is meV).

Atomization energy

Here, we calculated the RPA atomization energies of 50 molecules selected from the G-97 set. All molecular geometries were taken from Ref. 1. The computational details are described below. First, the total RPA energy of a molecule can be separated into the RPA correlation energy and the non-self-consistent HF total energy.

For the latter, we performed calculations in FHI-aims using the aug-cc-pwCV5Z basis set. The error in this part mainly originates from the basis-set incompleteness of the atomic orbitals used to describe the occupied states. To evaluate this error at the level of atomization energies, we performed calculations using aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets, and extrapolated the results to the CBS limit using a standard formula,

$$E_{HF}^{XY} = \frac{e^{-a\sqrt{Y}} E_{HF}^X - e^{-a\sqrt{X}} E_{HF}^Y}{e^{-a\sqrt{Y}} - e^{-a\sqrt{X}}} \quad (37)$$

In addition, calculations with the built-in Tier basis sets of FHI-aims were also performed for reference. These results are summarized in Tab. XI.

From Tab. XI, it is evident that the results obtained with the aug-cc-pwCV5Z basis set agree very well with both the extrapolated values and those based on the NAO basis. The data in the last row indicate that the HF contribution to the atomization energy obtained with the largest Gaussian basis differs from the extrapolated result by only 0.03 kcal/mol, and from the largest numerical atomic orbital (NAO) result by just 0.02 kcal/mol. This demonstrates that the aug-cc-pwCV5Z basis set provides a description of the occupied states that is already very close to the complete basis set (CBS) limit at the level of atomization energies. It also indicates that the choice of different types of atomic orbitals introduces very little scattering in the description of the occupied states.

For the RPA correlation energy, we solved the Delta-Sternheimer equation in the finite-element (FE) space to obtain the density-response matrix and the correlation energy. The main error sources here can be attributed to three aspects: (1) the FE grid density, (2) the RI approximation, and (3) the effect of basis-set errors in the occupied orbitals and energies on the RPA correlation energy when solving the Delta-Sternheimer equation. Convergence tests for all three sources are provided in Section 3 of the SI. The results show that the errors from the FE grid density and from the occupied-state orbitals and

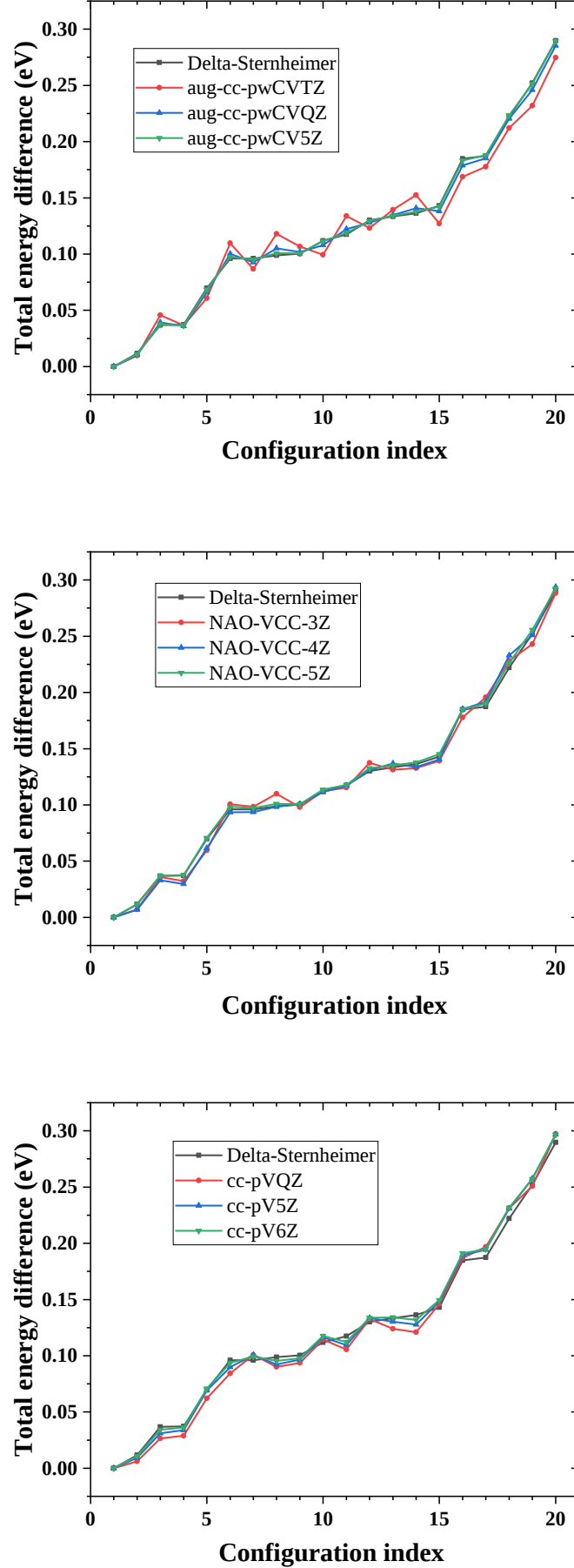


FIG. 5. The RPA total energy differences of 20 different configurations of the water dimer.

Energy part	aug-pwCVXZ			NAO-VCC-nZ			cc-pVXZ		
	TZ	QZ	5Z	3Z	5Z	5Z	QZ	5Z	6Z
RPA	7.01	2.69	0.78	5.85	4.30	1.16	7.49	5.45	3.95
HF	4.24	0.76	0.23	2.36	1.28	0.78	1.97	0.64	0.66
TOTAL	11.24	3.45	0.97	4.83	3.17	1.65	7.27	5.18	4.16

TABLE X. Comparison of basis set error for different basis sets. The energy unit is meV.

MO	QZ	5Z	Extrapolation	Tier	Δ -Extrapolation	Δ -Tier
CH ₄	-327.37	-327.50	-327.54	-327.49	0.04	0.01
C ₂ H ₂	-291.07	-291.20	-291.24	-291.21	0.04	0.01
C ₂ H ₄	-425.16	-425.32	-425.36	-425.33	0.05	0.01
C ₃ H ₆ (1)	-649.73	-649.95	-650.02	-649.96	0.06	0.01
C ₃ H ₆ (2)	-641.50	-641.72	-641.78	-641.72	0.06	0.00
C ₃ H ₄ (1)	-516.37	-516.55	-516.61	-516.57	0.05	0.02
C ₃ H ₄ (2)	-519.41	-519.60	-519.65	-519.62	0.05	0.02
C ₃ H ₄ (3)	-493.00	-493.18	-493.24	-493.21	0.05	0.02
C ₂ H ₆	-548.57	-548.77	-548.83	-548.76	0.06	0.01
CH ₂ O	-251.67	-251.71	-251.72	-251.71	0.01	0.00
CH ₃ OH	-365.21	-365.31	-365.34	-365.30	0.03	0.02
CH ₂ O ₂	-319.40	-319.40	-319.40	-319.37	0.00	0.03
C ₂ H ₂ O ₂	-407.97	-407.98	-407.98	-407.97	0.00	0.02
C ₂ H ₆ O	-590.32	-590.47	-590.51	-590.44	0.04	0.03
C ₂ H ₄ O(1)	-482.09	-482.19	-482.22	-482.17	0.03	0.02
C ₂ H ₄ O(2)	-452.68	-452.77	-452.80	-452.78	0.03	0.01
H ₂ O	-154.87	-154.87	-154.88	-154.88	0.00	0.00
H ₂ O ₂	-129.37	-129.36	-129.35	-129.31	0.00	0.05
CO ₂	-234.03	-233.97	-233.95	-233.94	0.02	0.03
NH ₃	-199.64	-199.71	-199.73	-199.70	0.02	0.00
N ₂ H ₄	-263.71	-263.81	-263.84	-263.79	0.03	0.02
HCN	-195.13	-195.20	-195.21	-195.19	0.02	0.01
C ₃ NH ₃	-525.11	-525.26	-525.31	-525.27	0.04	0.01
C ₂ NH ₅	-501.87	-502.03	-502.08	-502.03	0.05	0.01
CNH ₅	-413.16	-413.31	-413.35	-413.29	0.04	0.02
C ₂ N ₂	-280.52	-280.57	-280.59	-280.57	0.02	0.01
N ₂ O	-72.73	-72.74	-72.74	-72.68	0.00	0.06
CHF ₃	-299.01	-298.93	-298.90	-298.94	0.02	0.02
C ₂ H ₃ F	-410.40	-410.49	-410.51	-410.50	0.03	0.01
CH ₂ F ₂	-300.42	-300.43	-300.43	-300.42	0.00	0.01
NF ₃	-14.44	-14.34	-14.31	-14.30	0.03	0.04
C ₂ H ₃ OF	-486.04	-486.07	-486.08	-486.05	0.01	0.02
F ₂ O	55.73	55.75	55.76	55.80	0.01	0.04
COF ₂	-249.56	-249.50	-249.48	-249.48	0.02	0.02
C ₃ H ₈	-770.57	-770.82	-770.90	-770.81	0.08	0.01
C ₆ H ₆	-1015.40	-1015.67	-1015.75	-1015.73	0.08	0.06
H ₂ S	-128.41	-128.45	-128.46	-128.48	0.01	0.03
CS ₂	-156.04	-156.10	-156.11	-156.17	0.02	0.07
CH ₄ S	-347.43	-347.57	-347.61	-347.59	0.04	0.03
COS	-196.31	-196.33	-196.34	-196.36	0.01	0.03
SO ₂	-92.76	-92.85	-92.88	-92.75	0.03	0.10
HClO	-73.34	-73.35	-73.36	-73.33	0.00	0.03
CH ₃ Cl	-294.11	-294.23	-294.26	-294.22	0.03	0.01
NOCl	-27.15	-27.11	-27.09	-27.06	0.01	0.05
CH ₂ Cl ₂	-256.93	-257.00	-257.01	-257.04	0.02	0.04
C ₂ H ₃ Cl	-392.62	-392.75	-392.78	-392.77	0.04	0.02
C ₂ NH ₃	-427.34	-427.47	-427.51	-427.46	0.04	0.01
SiH ₄	-252.51	-252.62	-252.65	-252.66	0.03	0.04
PH ₃	-168.38	-168.45	-168.47	-168.47	0.02	0.02
BF ₃	-351.41	-351.26	-351.21	-351.31	0.04	0.06
MAE					0.03	0.02

TABLE XI. Atomization energy of non-SCF HF part for 50 molecules. The energy unit is kcal/mol. The second and third columns present results obtained with the aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets, respectively. The fourth column shows the CBS-extrapolated values obtained from the second and third columns using the two-point extrapolation formula (Eq. 37). The fifth column provides the results from the largest available tier basis set in FHI-AIMS (namely, tier4 plus additional basis functions). In the sixth and seventh columns, we report the absolute deviations of the aug-cc-pwCV5Z results from the extrapolated values and the NAO basis set results, respectively.

energies are both below the meV level, and thus negligible compared with the RI error. The RI approximation therefore constitutes the dominant source of error in this work. To minimize it, we employed auxiliary bases generated on-the-fly from aug-cc-pwCV5Z with $L_{\max} = 9$. Tests on diatomic molecules indicate that the average er-

ror at the level of atomization energies is only 0.04 kcal/mol. Since the RI error is expected to scale linearly with the number of atoms, it can be estimated as about 0.02 kcal/mol per atom. Taken together, after considering all possible error sources, we conclude that the dominant error in this work arises from the RI approxima-

tion, amounting to roughly 0.02 kcal/mol per atom. In Tab. XII, we report the total atomization energies of 50 molecules at the RPA level (including both the HF contribution and the RPA correlation contribution). These results can serve as reference data for future benchmarking studies and provide numerical standards for the development of correlation-consistent basis sets. In addition, to assess the basis set errors of finite-basis calculations, we present results obtained with the aug-cc-pwCV5Z basis set within the SOS framework. Furthermore, we report CBS-extrapolated results obtained by applying Eq. 37 for HF total energy part and Eq. 38 for RPA correlation energy part to the SOS results from aug-cc-pwCVQZ and aug-cc-pwCV5Z, which allow us to evaluate the accuracy of the extrapolation schemes.

$$E_{\text{corr}}^{\text{XY}} = \frac{X^3 E_{\text{corr}}^{\text{X}} - Y^3 E_{\text{corr}}^{\text{Y}}}{X^3 - Y^3} \quad (38)$$

From Tab. XII, it can be seen that the basis set error within the finite-basis SOS framework is 1.67 kcal/mol (for AE) and 1.70 kcal/mol (for FC). After extrapolation to the CBS limit using the extrapolation formula, the mean error is reduced to 0.34 kcal/mol (for AE) and 0.33 kcal/mol (for FC). This indicates that the extrapolation technique can indeed effectively reduce the basis set error. We also observe that the finite-basis results consistently underestimate the atomization energies, whereas the extrapolated results consistently overestimate them. We attribute this to the basis set superposition error (BSSE). In the calculations of Tab. XII, neither the finite-basis nor the extrapolated results account for BSSE, as the atomic energies were computed independently. To examine the influence of BSSE, we selected 10 molecules from Tab. XII and consider counterpoise (CP) correction to the BSSEs. The results are presented in Tab. XIII.

It can be seen that after the CP correction, the tendency of the extrapolated results to overestimate the atomization energies almost disappears. The mean error with respect to the results of this work is slightly reduced. The impact of the CP correction on finite-basis results is much larger than on extrapolated results, with the error increasing from 0.95 kcal/mol to 3.22 kcal/mol. Therefore, based on these results, for finite-basis calculations, the results obtained without the CP correction are more reliable. For results extrapolated to the basis-set limit, the CP correction can slightly improve accuracy.

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- [1] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
 - [2] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
 - [3] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (McGraw-Hill, New York, 1989).
 - [4] Martin, R. M., Reining, L., and Ceperley, D. M., *Interacting electrons: Theory and Computational Approaches* (Cambridge University Press, 2016).
 - [5] R. A. Friesner, Ab initio quantum chemistry: Methodology and applications, *Proc. Natl. Acad. Sci.* **102**, 6648 (2005).
 - [6] S. Ghosh, P. Verma, C. J. Cramer, L. Gagliardi, and D. G. Truhlar, Combining wave function methods with density functional theory for excited states, *Chemical Reviews* **118**, 7249 (2018), pMID: 30044618, <https://doi.org/10.1021/acs.chemrev.8b00193>.
 - [7] R. K. Nesbet, Configuration interaction in orbital theories, *Proc. R. Soc. Lond. A* **230**, 312 (1955).
 - [8] J. Čížek, On the correlation problem in atomic and molecular systems. calculation of wavefunction components in urself-type expansion using quantum-field theoretical methods, *J. Chem. Phys.* **45**, 4256 (1966).
 - [9] R. J. Bartlett and M. Musiał, Coupled-cluster theory in quantum chemistry, *Rev. Mod. Phys.* **79**, 291 (2007).
 - [10] L. Hedin, New method for calculating the one-particle green's function with application to the electron-gas problem, *Phys. Rev.* **139**, A796 (1965).
 - [11] D. Bohm and D. Pines, A collective description of electron interactions: Iii. coulomb interactions in a degenerate electron gas, *Physical Review* **92**, 609 (1953).
 - [12] C. Møller and M. S. Plesset, Note on an approximation treatment for many-electron systems, *Phys. Rev.* **46**, 618 (1934).
 - [13] T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
 - [14] K. A. Peterson, T. H. Dunning, and K. A. Wilson, Benchmark calculations with correlated molecular wave functions. iv. the classical barrier height of the $\text{h} + \text{h}_2 \rightarrow \text{h}_2 + \text{h}$ reaction, *J. Chem. Phys.* **112**, 111 (2000).
 - [15] Y. Zhang, C. Müller, D. Usvyat, M. Schütz, and C. Draxl, Numeric atom-centered orbital basis sets with valence-correlation consistency for correlated wavefunction methods, *J. Chem. Theory Comput.* **9**, 4517 (2013).
 - [16] T. Kato, On the eigenfunctions of many-particle systems in quantum mechanics, *Commun. Pure Appl. Math.* **10**, 151 (1957).
 - [17] W. Kutzelnigg, r_{12} -dependent terms in the wave function as closed sums of partial wave amplitudes for large l, *Theoretica Chimica Acta* **68**, 445 (1985).
 - [18] W. Kutzelnigg and W. Klopper, Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. i. general theory, *The Journal of Chemical Physics* **94**, 1985 (1991).
 - [19] V. Termath, W. Klopper, and W. Kutzelnigg, Wave func-

MO	This work AE	This work FC	5Z AE	5Z FC	Extrapolation AE	Extrapolation FC
CH ₄	-406.10	-404.93	-405.31 (0.79)	-404.17 (0.76)	-406.35 (-0.25)	-405.17 (-0.24)
C ₂ H ₂	-383.47	-381.02	-381.99 (1.49)	-379.61 (1.41)	-383.91 (-0.44)	-381.42 (-0.40)
C ₂ H ₄	-539.70	-537.41	-538.26 (1.44)	-536.04 (1.37)	-540.08 (-0.38)	-537.77 (-0.36)
C ₃ H ₆ (1)	-823.79	-820.43	-821.63 (2.16)	-818.30 (2.12)	-824.35 (-0.56)	-820.90 (-0.47)
C ₃ H ₆ (2)	-816.32	-815.37	-813.92 (2.40)	-810.59 (4.77)	-816.75 (-0.43)	-813.30 (2.07)
C ₃ H ₄ (1)	-668.66	-665.09	-666.58 (2.08)	-663.08 (2.00)	-669.08 (-0.42)	-665.44 (-0.35)
C ₃ H ₄ (2)	-669.82	-666.23	-667.62 (2.20)	-664.09 (2.14)	-670.32 (-0.50)	-666.64 (-0.41)
C ₃ H ₄ (3)	-647.45	-644.04	-645.19 (2.26)	-641.85 (2.19)	-647.88 (-0.42)	-644.40 (-0.36)
C ₂ H ₆	-686.11	-683.89	-684.54 (1.57)	-682.38 (1.51)	-686.51 (-0.40)	-684.26 (-0.37)
CH ₂ O	-356.97	-355.62	-355.69 (1.27)	-354.36 (1.26)	-357.17 (-0.21)	-355.79 (-0.17)
CH ₃ OH	-492.28	-490.92	-490.79 (1.49)	-489.44 (1.48)	-492.57 (-0.29)	-491.18 (-0.26)
CH ₂ O ₂	-475.22	-473.42	-473.18 (2.03)	-471.43 (1.99)	-475.51 (-0.30)	-473.70 (-0.28)
C ₂ H ₂ O ₂	-600.27	-597.52	-597.73 (2.54)	-595.02 (2.50)	-600.63 (-0.36)	-597.81 (-0.30)
C ₂ H ₆ O	-776.84	-774.42	-774.68 (2.16)	-772.25 (2.17)	-777.36 (-0.52)	-774.86 (-0.44)
C ₂ H ₄ O(1)	-646.31	-643.76	-644.21 (2.10)	-641.73 (2.04)	-646.68 (-0.37)	-644.10 (-0.34)
C ₂ H ₄ O(2)	-620.55	-618.25	-618.38 (2.17)	-616.04 (2.21)	-620.92 (-0.36)	-618.49 (-0.24)
H ₂ O	-223.57	-223.26	-222.99 (0.58)	-222.60 (0.66)	-223.90 (-0.34)	-223.51 (-0.25)
H ₂ O ₂	-256.30	-255.78	-255.10 (1.20)	-254.59 (1.19)	-256.48 (-0.18)	-255.98 (-0.20)
CO ₂	-366.44	-364.51	-364.59 (1.85)	-362.61 (1.90)	-366.76 (-0.32)	-364.70 (-0.19)
NH ₃	-291.30	-290.65	-290.54 (0.76)	-289.90 (0.75)	-291.59 (-0.29)	-290.93 (-0.28)
N ₂ H ₄	-427.91	-426.72	-426.26 (1.65)	-425.11 (1.61)	-428.22 (-0.31)	-427.04 (-0.32)
HCN	-300.54	-298.69	-299.19 (1.35)	-297.42 (1.27)	-300.81 (-0.27)	-298.96 (-0.27)
C ₃ NH ₃	-725.79	-721.71	-723.18 (2.61)	-719.15 (2.56)	-726.37 (-0.58)	-722.16 (-0.45)
C ₂ NH ₅	-691.54	-688.80	-689.16 (2.38)	-686.48 (2.32)	-691.95 (-0.41)	-689.18 (-0.38)
CNH ₅	-563.31	-561.65	-561.78 (1.53)	-560.12 (1.53)	-563.74 (-0.43)	-562.03 (-0.38)
C ₂ N ₂	-476.28	-472.61	-473.92 (2.36)	-470.30 (2.31)	-476.78 (-0.50)	-472.99 (-0.38)
N ₂ O	-259.68	-258.10	-257.83 (1.85)	-256.27 (1.82)	-259.84 (-0.16)	-258.24 (-0.14)
CHF ₃	-423.46	-422.28	-421.45 (2.01)	-420.28 (1.99)	-423.58 (-0.12)	-422.38 (-0.10)
C ₂ H ₃ F	-542.26	-539.87	-540.42 (1.84)	-538.08 (1.79)	-542.61 (-0.35)	-540.18 (-0.31)
CH ₂ F ₂	-409.97	-408.89	-408.42 (1.55)	-407.30 (1.59)	-410.19 (-0.22)	-409.04 (-0.15)
NF ₃	-183.91	-183.63	-182.35 (1.56)	-182.02 (1.61)	-183.95 (-0.04)	-183.64 (-0.01)
C ₂ H ₃ OF	-667.47	-664.80	-665.00 (2.47)	-662.38 (2.42)	-667.86 (-0.39)	-665.15 (-0.35)
F ₂ O	-78.95	-78.79	-77.96 (0.99)	-77.78 (1.01)	-78.98 (-0.03)	-78.81 (-0.02)
COF ₂	-386.78	-385.16	-384.65 (2.13)	-383.02 (2.14)	-386.92 (-0.15)	-385.25 (-0.09)
C ₃ H ₈	-967.94	-964.66	-965.64 (2.30)	-962.43 (2.23)	-968.52 (-0.58)	-965.19 (-0.53)
C ₆ H ₆	-1298.40	-1291.33	-1293.79 (4.61)	-1286.95 (4.38)	-1299.02 (-0.62)	-1291.92 (-0.59)
H ₂ S	-177.79	-177.06	-177.56 (0.23)	-176.87 (0.19)	-177.83 (-0.03)	-177.17 (-0.11)
CS ₂	-263.41	-260.62	-261.92 (1.49)	-259.40 (1.22)	-263.80 (-0.39)	-261.27 (-0.65)
CH ₄ S	-456.48	-454.85	-455.61 (0.87)	-453.92 (0.93)	-456.91 (-0.43)	-455.25 (-0.40)
COS	-315.45	-313.28	-314.02 (1.43)	-311.79 (1.49)	-315.97 (-0.52)	-313.68 (-0.40)
SO ₂	-243.33	-241.90	-241.49 (1.84)	-240.03 (1.87)	-243.69 (-0.36)	-242.25 (-0.35)
HClO	-155.02	-154.56	-154.18 (0.84)	-153.68 (0.88)	-155.16 (-0.14)	-154.69 (-0.13)
CH ₃ Cl	-377.24	-375.96	-376.33 (0.91)	-374.97 (0.99)	-377.61 (-0.37)	-376.25 (-0.29)
NOCl	-181.15	-180.24	-179.82 (1.33)	-178.91 (1.33)	-181.21 (-0.06)	-180.29 (-0.05)
CH ₂ Cl ₂	-347.74	-346.32	-346.76 (0.98)	-345.12 (1.20)	-348.21 (-0.47)	-346.61 (-0.29)
C ₂ H ₃ Cl	-514.50	-511.94	-512.92 (1.58)	-510.36 (1.58)	-514.98 (-0.48)	-512.37 (-0.43)
C ₂ NH ₃	-589.88	-586.93	-587.85 (2.03)	-584.93 (2.00)	-590.30 (-0.42)	-587.26 (-0.33)
SiH ₄	-316.27	-315.57	-316.10 (0.17)	-315.38 (0.19)	-316.57 (-0.30)	-315.94 (-0.36)
PH ₃	-239.39	-238.70	-239.30 (0.09)	-238.55 (0.15)	-239.60 (-0.22)	-238.93 (-0.23)
BF ₃	-435.64	-433.21	-433.51 (2.12)	-431.27 (1.94)	-436.08 (-0.45)	-433.49 (-0.28)
MAE	/	/	1.67	1.70	0.34	0.33

TABLE XII. The atomization energies of 50 molecules at the RPA level (including the HF contribution and the RPA correlation part) are reported. The second and third columns represent the AE and FC approximation atomization energies obtained in this work. The fourth and fifth columns show the AE and FC approximation atomization energies calculated with the aug-cc-pwCV5Z basis set. The sixth and seventh columns correspond to the extrapolated results obtained from the aug-cc-pwCVQZ and aug-cc-pwCV5Z data using Eq. 37 and Eq. 38, respectively. The energies are given in kcal/mol.

- tions with terms linear in the interelectronic coordinates to take care of the correlation cusp. ii. mp2-r12 calculations on closed-shell atoms, [The Journal of Chemical Physics](#) **94**, 2002 (1991).
- [20] W. Klopper and W. Kutzelnigg, Wave functions with terms linear in the interelectronic coordinates to take care of the correlation cusp. iii. mp2-r12 calculations on molecules of first-row atoms, [The Journal of Chemical](#)

- [Physics](#) **94**, 2020 (1991).
- [21] S. Ten-no, Initiation of explicitly correlated slater-type geminal theory, [Chem. Phys. Lett.](#) **330**, 169 (2000).
- [22] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, R12 methods in explicitly correlated molecular electronic structure theory, [International Reviews in Physical Chemistry](#) **25**, 427 (2006).
- [23] L. Kong, F. A. Bischoff, and E. F. Valeev, Explicitly cor-

MO	5Z(CP)	5Z	Extra(CP)	Extra	This work
H ₂ O	-221.80 (1.77)	-222.99 (0.58)	-223.58 (-0.01)	-223.90 (-0.33)	-223.57
NH ₃	-289.17 (2.13)	-290.54 (0.76)	-291.29 (0.00)	-291.59 (-0.29)	-291.30
CO ₂	-362.38 (4.06)	-364.59 (1.85)	-366.49 (-0.05)	-366.76 (-0.32)	-366.44
CH ₂ O	-353.93 (3.03)	-355.69 (1.27)	-356.89 (0.07)	-357.17 (-0.21)	-356.97
C ₂ H ₆	-681.87 (4.24)	-684.54 (1.57)	-686.04 (0.08)	-686.51 (-0.40)	-686.11
C ₃ H ₆ -2	-810.44 (5.88)	-815.37 (0.95)	-816.20 (0.12)	-816.75 (-0.43)	-816.32
C ₂ NH ₃	-584.71 (5.17)	-587.85 (2.02)	-589.83 (0.05)	-590.30 (-0.42)	-589.88
SiH ₄	-314.21 (2.06)	-316.10 (0.17)	-315.98 (0.29)	-316.57 (-0.30)	-316.27
PH ₃	-237.47 (1.92)	-239.30 (0.08)	-239.09 (0.29)	-239.60 (-0.22)	-239.39
H ₂ S	-175.90 (1.89)	-177.56 (0.23)	-177.41 (0.38)	-177.83 (-0.03)	-177.79
MAE	3.22	0.95	0.14	0.30	/

TABLE XIII. CP correction to the BSSEs for selected 10 molecules. The values in parentheses represent the differences with respect to the results obtained in the present work (last column). The energy unit is kcal/mol.

- related R12/F12 methods for electronic structure, Chemical reviews **112**, 75 (2012).
- [24] S. Ten-no, A feasible transcorrelated method for treating electronic cusps using a frozen gaussian geminal, *Chemical Physics Letters* **330**, 169 (2000).
- [25] C. Hättig, W. Klopper, A. Köhn, and D. P. Tew, Explicitly correlated electrons in molecules, *Chem. Rev.* **112**, 4 (2012).
- [26] S. Ten-no, Explicitly correlated second-order perturbation theory: Introduction of a rational generator and numerical quadratures, *The Journal of Chemical Physics* **121**, 117 (2004).
- [27] T. B. Adler, G. Knizia, and H.-J. Werner, A simple and efficient ccsd(t)-f12 approximation, *The Journal of Chemical Physics* **127**, 221106 (2007).
- [28] T. B. Adler and H.-J. Werner, An explicitly correlated local coupled cluster method for calculations of large molecules close to the basis set limit, *The Journal of Chemical Physics* **135**, 144117 (2011).
- [29] G. Knizia, T. B. Adler, and H.-J. Werner, Simplified ccsd(t)-f12 methods: Theory and benchmarks, *The Journal of Chemical Physics* **130**, 054104 (2009).
- [30] M. Humer, M. E. Harding, M. Schlipf, A. Taheridehkordi, Z. Sukurma, W. Klopper, and G. Kresse, Approaching the basis-set limit of the dRPA correlation energy with explicitly correlated and projector augmented-wave methods, *J. Chem. Phys.* **157** (2022).
- [31] J. R. Chelikowsky, N. Troullier, and Y. Saad, Finite-difference pseudopotential method: Electronic structure calculations without a basis, *Physical Review Letters* **72**, 1240 (1994).
- [32] J. E. Pask and P. A. Sterne, Finite element methods in ab initio electronic structure calculations, *Modelling and Simulation in Materials Science and Engineering* **13**, R71 (2005).
- [33] L. Genovese, A. Neelov, S. Goedecker, T. Deutsch, S. A. Ghasemi, A. Willand, D. Caliste, O. Zilberberg, M. J. Rayson, A. Bergman, and R. Schneider, Daubechies wavelets as a basis set for density functional pseudopotential calculations, *The Journal of Chemical Physics* **129**, 014109 (2008).
- [34] J. R. Flores, High-precision atomic computations from finite element techniques: Second-order correlation energies of rare gas atoms, *The Journal of Chemical Physics* **98**, 5642 (1993).
- [35] J. R. Flores and P. Redondo, High-precision atomic computations from finite element techniques: Second-order correlation energies for be, ca, sr, cd, ba, yb, and hg, *Journal of Computational Chemistry* **15**, 782 (1994).
- [36] J. S. Kottmann and F. A. Bischoff, Coupled-cluster in real space. 1. cc2 ground state energies using multiresolution analysis, *Journal of Chemical Theory and Computation* **13**, 5945 (2017), pMID: 28902997, <https://doi.org/10.1021/acs.jctc.7b00694>.
- [37] J. S. Kottmann and F. A. Bischoff, Coupled-cluster in real space. 2. cc2 excited states using multiresolution analysis, *Journal of Chemical Theory and Computation* **13**, 5956 (2017), pMID: 28902991, <https://doi.org/10.1021/acs.jctc.7b00695>.
- [38] J. S. Kottmann and F. A. Bischoff, Wavelets meet many-body theory: The correlation energy of the helium atom, *Journal of Chemical Theory and Computation* **13**, 594 (2017).
- [39] J. S. Kottmann and F. A. Bischoff, Wavelet-based second-order möller-plesset perturbation theory: Towards basis set limit correlation energies with multiresolution analysis, *Molecular Physics* **115**, 1606 (2017).
- [40] H. Peng, S. Yang, H. Jiang, H. Weng, and X. Ren, Basis-set-error-free random-phase approximation correlation energies for atoms based on the sternheimer equation, *J. Chem. Theory Comput.* **19**, 7199 (2023).
- [41] H. Peng and X. Ren, Ab initio correlated calculations without finite basis-set error: Numerically precise all-electron rpa correlation energies for diatomic molecules, arXiv preprint arXiv:2411.01941 (2024).
- [42] M. Betzinger, C. Friedrich, A. Görling, and S. Blügel, Precise response functions in all-electron methods: Application to the optimized-effective-potential approach, *Phys. Rev. B* **85**, 245124 (2012).
- [43] M. Betzinger, C. Friedrich, and S. Blügel, Precise response functions in all-electron methods: Generalization to nonspherical perturbations and application to nio, *Phys. Rev. B* **88**, 075130 (2013).
- [44] M. Betzinger, C. Friedrich, A. Görling, and S. Blügel, Precise all-electron dynamical response functions: Application to COHSEX and the RPA correlation energy, *Phys. Rev. B* **92**, 245101 (2015).
- [45] R. Ramakrishnan, P. O. Dral, M. Rupp, and O. A. von

- Lilienfeld, Big data meets quantum chemistry approximations: The Δ -machine learning approach, *Journal of Chemical Theory and Computation* **11**, 2087 (2015).
- [46] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, and J. A. Pople, Gaussian-3 (g3) theory for molecules containing first and second-row atoms, *The Journal of chemical physics* **109**, 7764 (1998).
- [47] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler, Ab initio molecular simulations with numeric atom-centered orbitals, *Comput. Phys. Commun.* **180**, 2175 (2009).
- [48] T. H. Dunning Jr, Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen, *J. Chem. Phys.* **90**, 1007 (1989).
- [49] K. A. Peterson and T. H. Dunning Jr, Accurate correlation consistent basis sets for molecular core–valence correlation effects: The second row atoms al–ar, and the first row atoms b–ne revisited, *J. Chem. Phys.* **117**, 10548 (2002).
- [50] R. Haunschild and W. Klopper, New accurate reference energies for the g2/97 test set, *The Journal of chemical physics* **136** (2012).
- [51] X. Ren, P. Rinke, V. Blum, J. Wieferink, A. Tkatchenko, A. Sanfilippo, K. Reuter, and M. Scheffler, Resolution-of-identity approach to Hartree–Fock, hybrid density functionals, RPA, MP2 and GW with numeric atom-centered orbital basis functions, *New J. Phys.* **14**, 053020 (2012).
- [52] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [53] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [54] Y. Liao, H. Liu, Z. Guan, and H. Xie, *Openpfem: A finite element library based on distributed mesh parallel communication* (2025), chinaXiv preprint, [ChinaXiv:202506.00011](https://arxiv.org/abs/202506.00011).
- [55] W. Dörfler, A convergent adaptive algorithm for poisson’s equation, *SIAM Journal on Numerical Analysis* **33**, 1106 (1996).
- [56] S. Balay, S. Abhyankar, M. F. Adams, J. Brown, P. Brune, K. Buschelman, L. Dalcin, A. Dener, V. Eijkhout, W. D. Gropp, D. Karpeev, D. Kaushik, M. G. Knepley, D. A. May, L. C. McInnes, R. T. Mills, T. Munson, K. Rupp, P. Sanan, B. F. Smith, S. Zampini, and H. Zhang, *PETSc/TAO Users Manual*, Tech. Rep. ANL-21/39 - Revision 3.19 (Argonne National Laboratory, 2024).