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A simple self-interaction correction to RPA-like correlation energies

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Abstract

The random phase approximation (RPA) is exact for the exchange energy of a many-electron ground state, but RPA makes the correlation energy too negative by about 0.5 eV/electron. That large short-range error, which tends to cancel out of iso-electronic energy differences, is largely corrected by an exchange-correlation kernel, or (as in RPA+) by an additive local or semilocal correction. RPA+ is by construction exact for the homogeneous electron gas, and it is also accurate for the jellium surface. RPA+ often gives realistic total energies for atoms or solids in which spin-polarization corrections are absent or small. RPA and RPA+ also yield realistic singlet binding energy curves for H₂ and N₂, and thus RPA+ yields correct total energies even for spin-unpolarized atoms with fractional spins and strong correlation, as in stretched H₂ or N₂. However, RPA and RPA+ can be very wrong for spin-polarized one-electron systems (especially for stretched H₂⁺), and also for the spin-polarization energies of atoms. The spin-polarization energy is often a small part of the total energy of an atom, but important for ionization energies, electron affinities, and the atomization energies of molecules. Here we propose a computationally efficient *generalized* RPA+ (gRPA+) that changes RPA+ only for spin-polarized systems by making gRPA+ exact for all one-electron densities, in the same simple semilocal way that the correlation energy densities of many meta-generalized gradient approximations are made self-correlation free. By construction, gRPA+ does not degrade the exact RPA+ description of jellium. gRPA+ is found to greatly improve upon RPA and RPA+ for the ionization energies and electron affinities of light atoms. Many versions of RPA with an approximate exchange-correlation kernel fail to be exact for all one-electron densities, and they can also be self-interaction corrected in this way.

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I. Introduction

For correlation energies, the random-phase approximation (RPA)^{1,2} has attracted significant attention over the past decade or two due to its ability to treat different types of interactions (e.g., dispersion, metallic, covalent and ionic interactions) seamlessly, at a cost that is tractable for moderately large systems **with about 15 heavy atoms**. For this reason, RPA has been used to provide “silver standard” benchmarking for electronic systems where more refined (and thus expensive) approaches are intractable³⁻⁷.

RPA is typically used as a post-density-functional-theory (DFT) method for calculating energies. That is, one first performs an approximate DFT calculation, e.g., using the Perdew-Burke-Ernzerhof⁸ (PBE) functional, and then uses the resulting orbitals and their energies to calculate the non-interacting (Kohn-Sham) response function χ_0 , and from it the RPA correlation energy

$$E_{cRPA} = \int_0^1 d\lambda \int \frac{drdr'}{2|r-r'|} n_{2c,\lambda}^{RPA}(\mathbf{r}, \mathbf{r}') , \quad (1)$$

where $n_{2c,\lambda}^{RPA} = \int_0^\infty \frac{d\omega}{\pi} [\chi_\lambda - \chi_0]$ is the contribution to the pair-density from Coulomb correlation. The random-phase approximation involves approximating the interacting response function as $\chi_\lambda = \chi_0 + \lambda \chi_0 * U * \chi_\lambda$. Stars indicate convolution over interior variables and $U = 1/|\mathbf{r}-\mathbf{r}'|$ is the Coulomb potential. We can also rewrite (1) as an integral

$$E_{cRPA} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{cRPA}(\mathbf{r}) \quad (2)$$

over a correlation energy density. Here $n = n_\uparrow + n_\downarrow$ is the electron density. The correlation energy per electron at \mathbf{r} is

$$\epsilon_{cRPA}(\mathbf{r}) = \int \frac{dr'}{2|r-r'|} \int_0^1 d\lambda \frac{n_{2,\lambda}^{RPA}(\mathbf{r}, \mathbf{r}')}{n(\mathbf{r})} . \quad (3)$$

RPA typically does a decent job of estimating energy differences between similar species, such as the interactions between two-dimensional layers **with a maximal error of 4%**⁴. RPA yields reasonable structural properties for non-magnetic solids with **a mean absolute relative error of 0.4% and 4% for lattice constants and bulk moduli respectively**,⁹ and captures the static correlation in the dissociating H_2 ^{10,11}. It does a much poorer job of treating absolute energies, or of

predicting energies where the fundamental properties of the different species are different^{6,7,12,13}. For example, while RPA makes 0% relative error for the correlation energy in the high-density limit of the uniform gas, it makes the correlation energy per electron too negative by about 0.5 eV or 11.5 kcal/mol^{1,2}. A similar result holds for atoms¹⁴. Furthermore, the failure of RPA for dissociating H_2^+ is dramatic¹⁵. Perhaps most disappointing has been the performance^{9,12} of RPA for the atomization energies of molecules, which is not better than that of the much less expensive PBE generalized gradient approximation⁸.

Significant work has been dedicated to improving energies by modelling the exchange and correlation kernel $f_{xc}^\lambda(\mathbf{r}, \mathbf{r}'; \omega)$ that, when added to the Coulomb interaction $\lambda U(\mathbf{r}' - \mathbf{r})$, would in principle make RPA exact via the introduction of a properly-screened or damped electron-electron interaction (e.g., refs. 16–21). Alternatively, the correlation energy can be also obtained with the exact exchange kernel within the time-dependent exact exchange (TDEXX) or time-dependent Hartree-Fock (TDHF) formalism²²⁻²⁴. The short-range correlation of RPA can be improved by the range-separation framework²⁵. Besides the standard particle-hole RPA, there is also a self-correlation-free particle-particle RPA²⁶. Such “beyond-RPA” methods often offer some improvement over RPA, but have the unfortunate property of typically being much more computationally demanding than RPA.

An alternate and low-cost route to overcome this shortcoming was provided by Kurth and Perdew²⁷. They recognised that the main source of error in the RPA energy was from short-ranged correlations, which could be corrected locally. They thus proposed that the overall correlation energy could be improved by setting

$$E_{CRPA+} = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{CRPA+}(\mathbf{r}), \quad (4)$$

$$\epsilon_{CRPA+}(\mathbf{r}) = \epsilon_{CRPA}(\mathbf{r}) + \epsilon_{CLSDA}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) - \epsilon_{CLRPA}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) , \quad (5)$$

to provide a local correction to the RPA energy based on its error for the homogeneous electron gas. Here, the local spin density approximation (LSDA) and LRPA energies are taken from the homogeneous electron gas using respectively exact and RPA correlation energies per electron, as parametrised in ref. 28.

Using (4) yields more accurate correlation energies for many systems. Unfortunately, it does not offer significant improvements to reaction energies when the reactants differ significantly from the products, especially when the effective number of electrons changes. This lack of success reflects

non-systematic errors in how the semi-local correction improves the properties of fundamentally different systems, such as neutrals and their ions.

In this work, we thus propose a straightforward modification to (4), that significantly improves its treatment of ionization energies and electron affinities, and improves its overall accuracy. This involves calculating a new self-interaction corrected generalized RPA+ (gRPA+) energy expression:

$$(6)$$

where $g(\zeta, y)$ is a meta-GGA²⁹-like damping factor that zeroes out the correlation energy density in one-electron regions. We further test two formulas for $g(\zeta, y)$. Both depend upon the spin-polarization function $\zeta = \frac{n_{\uparrow} - n_{\downarrow}}{n}$. The first model, $g_1(\zeta, z)$, also depends on the ratio

$$\text{---}, \quad (7a)$$

and was suggested in a similar context by Vydrov *et al* [30]. The second model $g_2(\zeta, \beta)$ also depends on the switching variable

$$\text{---} \quad (7b)$$

that indicates when a system is one- or two-electron like ($\beta \rightarrow 0$), homogeneous electron gas or HEG-like ($\beta \approx 1/2$), or involves overlapping shells ($\beta \rightarrow 1$)³¹. Here, τ_W is the positive orbital kinetic energy density that depends on the occupied Kohn-Sham orbitals $\tau_W = |\nabla n|^2/8n$ is the von Weizsaecker approximation, which is exact for one- and two-electron densities; and $\tau_{\text{HEG}} = (3/10)(3\pi^2)^{2/3}n^{5/3}$ is the Thomas-Fermi kinetic energy approximation, which is exact for uniform densities.

In the next section we detail two models for the factor --- in Eq. (4), and justify them on physical and practical grounds. Then, we apply them to various tests.

II. MODEL FOR THE FACTOR --- IN EQ. (6); IONIZATION POTENTIALS OF ATOMS

gRPA+ seeks to improve RPA+ by modifying the RPA+ correlation energy density locally. Before presenting our models for the damping factor --- , we summarize what is known:

1. RPA+ often works well when a system is spin-unpolarized ($\zeta = 0$), where we expect $g = 1$;
2. The correlation energy density should vanish in one-electron regions (with $z \approx 1$, $\beta \approx 0$ and ≈ 1), where we expect $g = 0$;

3. RPA+ is exact when the system is HEG-like (with $z = 0$ or $\beta \approx 1/2$), and thus we expect $g = 1$ in HEG-like regions;
4. Intermediate-range van der Waals interactions²⁹ occur in density-overlap regions where β is close to 1, so we expect $g = 1$ there.

Two simple models that accommodate these various physical conditions are

$$g_1(\zeta, z) = 1 - \zeta^2(2z^2 - z^3)^{c_1} \quad (8a)$$

$$g_2(\zeta, \beta) = 1 - \zeta^2 h(\beta), \quad (8b)$$

provided $c_1 > 0$; or $h(\beta = 0) = 1$ and $h(1/2) = 0$. Analyticity implies that c_1 must be integer, and the specific form is chosen to ensure exactness of leading terms in the gradient expansion. Smoothness of h is another desirable property, both for computational and physical reasons. One such model h that meets the desired criteria is

$$h(\beta) = \begin{cases} \exp\left(-\frac{c_2\beta}{\frac{1}{2}-\beta}\right), & \beta \leq \frac{1}{2} \\ 0 & \beta > \frac{1}{2} \end{cases} \quad (9)$$

Here $c_2 > 0$ is a parameter, and $c_2 \rightarrow \infty$ recovers RPA+. For non-zero ζ , this model gives maximum modification of RPA+ at $\beta = 0$, and no modification for HEG-like regions or in regions where shells overlap. Neither model introduces additional damping in unpolarized systems, as $\zeta=0$ there.

With the models chosen, we must select values of c that makes them work effectively. Our goal is to remove non-systematic errors. So, to choose c , we seek to minimize the mean absolute error (MAE) of the correlation contribution to the ionization potentials of various atoms, specifically Be, C, N, O, F and Na, subject to reasonable constraints. That is, we define

$$MAE_{IP}^m = \frac{1}{6} \sum_{Z \in \{4,6,7,8,9,11\}} |IP_c^{gRPA+}(Z) - IP_c^{\text{exact}}(Z)| \quad (10)$$

for valid values of c , using model g_m ; then seek to find optimal values $c_m^{\text{opt}} = \text{argmin } MAE_{IP}^m(c_m)$. Here $IP_c(Z) = E_c(Z, Z-1) - E_c(Z, Z)$ where $E_c^{\text{exact}}(Z, N)$ is the exact correlation energy of N electrons in a nuclear potential $-Z/r$, and $E_c^{gRPA+}(Z, N)$ is its equivalent calculated using Eq. (8a) or (8b) in Eq. (6). Exact values for IP_c are taken from the configuration interaction calculations of Chakravorty et al³².

Our calculations are carried out in the atomic code pyAtom, which is a python/scipy/numpy implementation of DFT in spherical geometries. We construct the Kohn-Sham orbitals and energies of the atoms and atomic ions using a spherically-symmetric Kohn-Sham potential produced by

ensemble averaging the KLI approximation³³ to exact exchange^{14,34}. These are used to reproduce, by construction, correct density variables (e.g., ρ) and other properties (e.g., ϵ) of both closed-shell and open-subshell cases. The Kohn-Sham equations and response equations are solved on a radial mesh. This approach has previously been shown to reproduce well the properties of atoms^{14,35}. We note that many applications of RPA use PBE orbitals. However, for atoms (and presumably cations), KLI gives results very close to calculations using the exact potential, and quite close to those from PBE¹⁴. Crucially, KLI also allows calculations of anions. The code is available on request.

Our tests indicate that, for g_1 , the minimum value of $\text{MAE}_{\text{IP}^1}(\zeta)$ is 3.2 kcal/mol – found for $\zeta = 0.8$. Since we require ζ to be integer, to make g_1 analytic, we set $c_1 = 1$. This introduces very little additional error to our benchmarking set, giving $\text{MAE}_{\text{IP}^1}(c_1=1) = 3.5$ kcal/mol.

Our tests also indicate that, using g_2 , $\text{MAE}_{\text{IP}^2}(\zeta)$ attains its minimum 3.2 kcal/mol for $\zeta \rightarrow 0^+$. However, setting $c_2 = 0$ is unphysical as it corresponds to a step function for β . We thus choose instead the value $\zeta = 0.2$, which gives an error less than 0.5 kcal/mol above the absolute minimum but which retains a physically reasonable form for β , as shown in Figure 1. It thus attains a good balance between physical constraints and error mitigation.

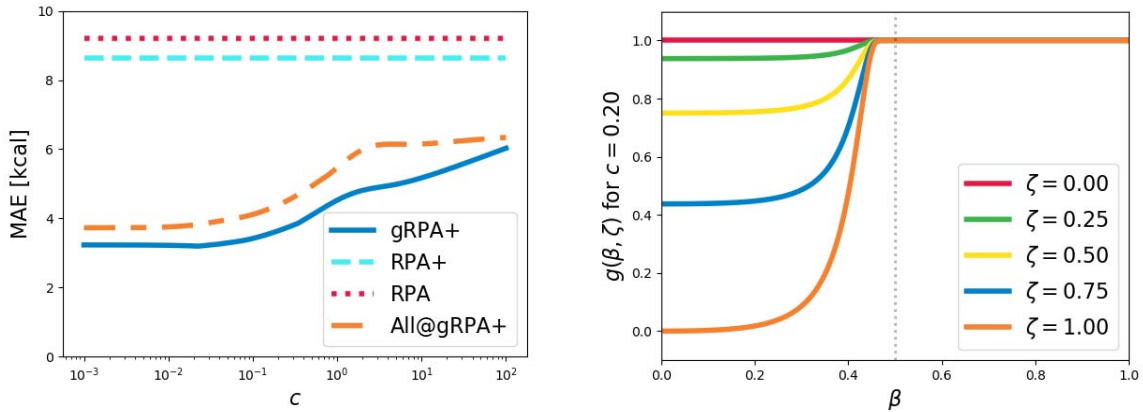


FIG. 1. MAE of IPs as a function of c (left), for RPA, RPA+ and gRPA+ (also shown, MAE for all correlation energies); and the damping factor $g(\beta, \zeta)$ (right) of Eqs. (6) and (8b), using $\zeta = 0.2$. The vertical line shows $\beta=0.5$.

Using $\zeta = 0.2$ gives $\text{MAE}_{\text{IP}^2}(\zeta=0.2) = 3.6$ kcal/mol, just 0.1 kcal/mol above the value found using g_1 with $\zeta=1$. This indicates that the precise details of the damping factor have some flexibility, a feature which might be exploited in future. For comparison, the equivalent error in RPA+ is 8.6 kcal/mol, more than twice as large and only a tiny improvement on RPA, with 9.2

kcal/mol. This is despite the fact that RPA+ improves absolute energies significantly (see later discussion). Thus, introducing the damping factor has the desired effect of significantly improving results for energy differences between unlike systems. Values for IP_c for the systems used in the optimization, and their errors under the different methods, are reported in Table I.

TABLE I. Correlation contributions IP_c to ionization potentials IP and their errors for RPA, RPA+ and gRPA+ using $c_1^{opt} = 1$ and $c_2^{opt} = 0.2$. All energies in kcal/mol. Mean absolute errors (MAE) are also reported.

Element	IP_c		Error		
	Exact	RPA	RPA+	gRPA+ (g_1)	gRPA+ (g_2)
Be	29.4	8.2	17.4	8.1	7.8
C	11	8.1	-3.8	-5.4	-5.3
N	13.6	15.3	1.5	0.6	1.5
O	40.2	-0.9	-10.6	-5.9	-6.2
F	40.2	9.1	-2.7	-0.5	-0.9
Na	3.8	13.5	-15.8	-0.4	0.3
MAE		9.2	8.6	3.5	3.6

III. ELECTRON AFFINITIES OF ATOMS; CORRELATION ENERGIES OF ATOMS AND IONS

Table II tests gRPA+ for correlation contributions $EA_c(Z) = E_c(Z, Z) - E_c(Z, Z + 1)$ to the electron affinities EA of the atoms studied in Table I. (See also ref. 34.) The results are qualitatively like those for the ionization potentials in Table I, suggesting that gRPA+ is not skewed to electron removal, but can also handle the generally more difficult case of electron addition. Both Tables show that, where the errors of RPA+ are large, they are corrected by gRPA+. But where the errors of RPA+ are small, they are sometimes slightly smaller than those of gRPA+.

TABLE II. Correlation contributions EA_c to electron affinities EA and their errors for RPA, RPA+ and gRPA+ with $c_1^{opt} = 1$ and $c_2^{opt} = 0.2$. All energies in kcal/mol. Mean absolute errors (MAE) are also reported.

Element	EA_c		Error		
	Exact	RPA	RPA+	gRPA+ (g_1)	gRPA+ (g_2)
C	16.6	16.1	-1.6	1.2	2.6
N	44.7	-1.3	-8.8	-5.4	-5.8
O	45.9	8.1	-2.8	-0.7	-1.1
F	47.1	17.0	5.8	6.4	6.3
Na	15.0	9.7	21.4	6.0	5.4
MAE		10.4	8.1	3.9	4.2

We now take our optimized damping factors g of Eqs. (6) and (8), and apply them to a larger set of atoms and ions to see how well they work. We expand our set of elements to include Mg, Al and P, and include double and triple cations as well as some anions in our tests. Results for the total correlation energy are shown in Figure 2, and values are reported in Table III.

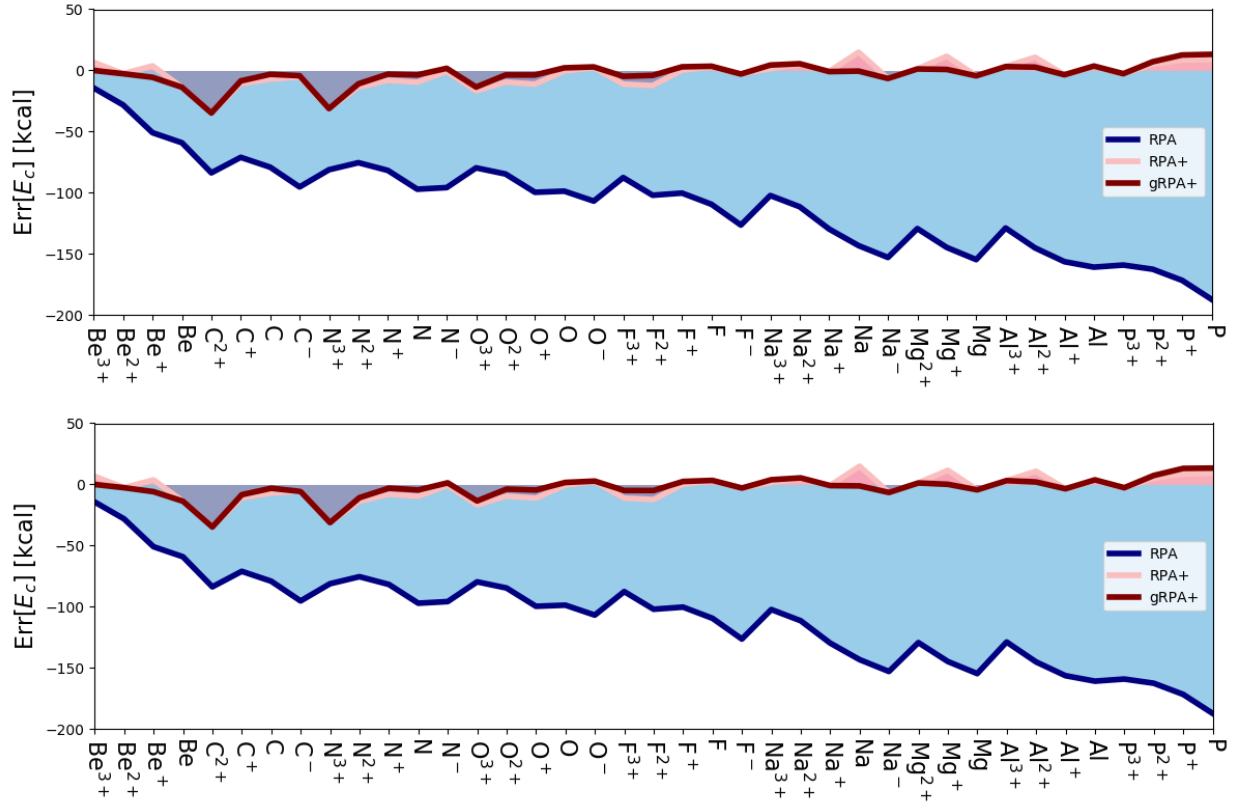


FIG. 2. Correlation energy errors (kcal/mol) for the full set of atoms and ions, using the models g_1 (top) and g_2 (bottom) [i.e., using Eqs (8a) and (8b) in Eq. (6), with $\alpha = 1$ and $\beta = 1$]

It is immediately clear from the figure that the greatest improvement to energies comes from RPA+. However, RPA+ correlation energies are fairly jagged across cations of the same species, which leads to non-systematic errors once energy differences are considered. gRPA+, while imperfect, tends to smooth out these errors and thus reduces the error in ionization potentials and electron affinities.

It is apparent from Table III that the gRPA+ approximation works best for atoms with open shells. This is the case for carbon, nitrogen and sodium.

Interesting errors, which cannot be fixed by gRPA+, are those for the Be isoelectronic series: Be, C^{2+} and N^{3+} in our set. In all these cases RPA+ deviates from its usual ability to correct closed shells well. We speculate that this might reflect that the near-degeneracy of $2s$ and $2p$ orbitals is inadequately captured in the uncorrected long-range part of RPA.

TABLE III. Correlation energy E_c and errors for RPA, RPA+ and gRPA+ with $c_1^{opt} = 1$ and $c_2^{opt} = 0.2$. All energies in kcal/mol.

	Z	N	E_c		Error			
			Exact	gRPA+	RPA	RPA+	gRPA+ (g_1)	gRPA+ (g_2)
Be ³⁺	4	1	0.0	0.0	-14.3	6.6	0.0	0.0
Be ²⁺	4	2	-27.6	-30.3	-28.1	-2.6	-2.6	-2.6
Be ⁺	4	3	-29.7	-35.8	-51.0	3.6	-5.6	-6.0
Be	4	4	-59.2	-73.0	-59.2	-13.8	-13.7	-13.8
C ²⁺	6	4	-69.9	-104.6	-83.6	-34.8	-34.8	-34.8
C ⁺	6	5	-87.1	-95.5	-71.0	-10.9	-8.5	-8.4
C	6	6	-98.2	-101.2	-79.0	-7.0	-3.1	-3.1
C ⁻	6	7	-114.8	-120.5	-95.1	-5.4	-4.3	-5.7
N ³⁺	7	4	-88.2	-119.3	-81.1	-31.2	-31.2	-31.2
N ²⁺	7	5	-94.5	-105.2	-75.3	-13.7	-10.9	-10.8
N ⁺	7	6	-104.6	-107.6	-81.7	-8.1	-3.0	-3.0
N	7	7	-118.2	-122.7	-97.0	-9.6	-3.6	-4.5
N ⁻	7	8	-162.9	-161.6	-95.7	-0.8	1.8	1.3
O ³⁺	8	5	-101.0	-114.5	-79.6	-16.7	-13.6	-13.5
O ²⁺	8	6	-109.8	-113.6	-84.6	-9.5	-3.7	-3.8
O ⁺	8	7	-121.8	-126.3	-99.5	-11.2	-3.7	-4.5
O	8	8	-161.9	-160.3	-98.6	-0.5	2.2	1.7
O ⁻	8	9	-207.8	-205.0	-106.7	2.3	2.9	2.8
F ³⁺	9	6	-114.2	-119.1	-87.5	-11.2	-4.8	-4.9
F ²⁺	9	7	-124.9	-129.8	-101.9	-12.3	-4.0	-4.9
F ⁺	9	8	-163.8	-161.3	-100.2	0.2	3.0	2.5
F	9	9	-204.0	-200.7	-109.3	2.9	3.5	3.3
F ⁻	9	10	-251.0	-254.0	-126.3	-2.9	-2.9	-2.9
Na ³⁺	11	8	-168.2	-164.3	-102.2	1.4	4.4	3.9
Na ²⁺	11	9	-205.2	-199.9	-111.3	4.9	5.5	5.4
Na ⁺	11	10	-244.1	-245.1	-129.6	-0.9	-0.9	-0.9
Na	11	11	-247.9	-249.1	-143.1	14.8	-0.5	-1.2
Na ⁻	11	12	-262.9	-269.5	-152.8	-6.6	-6.6	-6.6
Mg ²⁺	12	10	-244.8	-243.5	-129.2	1.2	1.2	1.2
Mg ⁺	12	11	-251.0	-250.9	-144.6	11.5	0.8	0.1
Mg	12	12	-274.9	-279.3	-154.5	-4.4	-4.4	-4.4
Al ³⁺	13	10	-245.4	-242.2	-128.7	3.2	3.2	3.2
Al ²⁺	13	11	-254.2	-252.2	-145.0	10.7	2.7	2.0
Al ⁺	13	12	-283.7	-287.2	-156.2	-3.5	-3.5	-3.5
Al	13	13	-295.0	-291.2	-160.7	3.1	3.6	3.8
P ³⁺	15	12	-296.2	-298.9	-159.0	-2.7	-2.7	-2.7
P ²⁺	15	13	-313.2	-305.8	-162.4	4.9	7.1	7.4
P ⁺	15	14	-327.6	-314.5	-171.5	8.5	12.7	13.1
P	15	15	-338.9	-325.5	-187.0	9.0	13.2	13.4
MAE					108.8	7.9	6.2	6.2

CONCLUSIONS

Our results and previous ones suggest that RPA+ correlation energy densities are often accurate for spin-unpolarized density regions ($|\zeta| = 0$) and for density regions in which various orbital shapes are strongly overlapped ($\beta > 0.4$), but not for density regions that are nearly one-electron-like. For the latter regions, we have proposed a self-interaction corrected or generalized RPA+ (gRPA+). We have shown that gRPA+ greatly improves the ionization potentials and electron affinities of atoms, in which spin-polarization effects play an important role. This success seems, at least in the atomic systems we tested, to be only weakly dependent on the specific model employed. In future work, we plan to build this self-interaction correction into a molecular code to test it for atomization energies, where spin-polarization effects are also important, and where choice of model might prove to be more important. Table III shows that for most spin-polarized neutral atoms the gRPA+ correlation energies are less negative than the RPA+ values, and this goes in the right direction to reduce the RPA+ underbinding¹² of molecules.

In the RPA+ correlation energy density, the RPA term and its local short-range correction term need the same kinds of damping factors, but the c parameters could be allowed to differ from one term to the other. The integrand of the RPA double integral is symmetric under interchange of \mathbf{r} and \mathbf{r}' , and, while our choice of Eq. (6) is equivalent to a symmetrized damping factor $[g(\mathbf{r}) + g(\mathbf{r}')]/2$, another possibility is $\sqrt{g(\mathbf{r})g(\mathbf{r}')}$. We will investigate these possibilities in future work.

The version of RPA+ we have employed here is one in which the correction to RPA is evaluated in the local spin-density approximation (LSDA). There is also a sophisticated generalized gradient approximation version³⁶ of RPA+. It is numerically close to the simpler LSDA, and will also be tested in future work.

The computational demands of RPA, RPA+, and gRPA+ were nearly the same in our work. We suspect that gRPA+ should be obtainable at a cost similar to that of resolution-of-the-identity based RPA implementations.

Exchange-correlation kernel corrections to RPA can be more accurate but more expensive than RPA+. They can also be self-interaction corrected via our general approach.

In summary, the generalized RPA+ (gRPA+) seems to retain the advantages of RPA while adding the benefits of being exact for slowly-varying and one-electron densities. In comparison to RPA+, gRPA+ can provide a better description of the spin-polarization energy that is important in many atoms and atomic ions. gRPA+ ionization energies and electron affinities of atoms are

strongly improved over RPA and RPA+. Further work will show if the RPA atomization-energy puzzle, which was not solved by RPA+, is finally solved by gRPA+.

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