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The RPA Atomization Energy Puzzle

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Abstract: There is current interest in the random phase approximation (RPA), a “fifth-rung” density functional for the exchange–correlation energy. RPA has full exact exchange and constructs the correlation with the help of the unoccupied Kohn–Sham orbitals. In many cases (uniform electron gas, jellium surface, and free atom), the correction to RPA is a short-ranged effect that is captured by a local spin density approximation (LSDA) or a generalized gradient approximation (GGA). Nonempirical density functionals for the correction to RPA were constructed earlier at the LSDA and GGA levels (RPA+), but they are constructed here at the fully nonlocal level (RPA++), using the van der Waals density functional (vdW-DF) of Langreth, Lundqvist, and collaborators. While they make important and helpful corrections to RPA total and ionization energies of free atoms, they correct the RPA atomization energies of molecules by only about 1 kcal/mol. Thus, it is puzzling that RPA atomization energies are, on average, about 10 kcal/mol lower than those of accurate values from experiment. We find here that a hybrid of 50% Perdew–Burke–Ernzerhof GGA with 50% RPA+ yields atomization energies much more accurate than either one does alone. This suggests a solution to the puzzle: While the proper correction to RPA is short-ranged in some systems, its contribution to the correlation hole can spread out in a molecule with multiple atomic centers, canceling part of the spread of the exact exchange hole (more so than in RPA or RPA+), making the true exchange–correlation hole more localized than in RPA or RPA+. This effect is not captured even by the vdW-DF nonlocality, but it requires the different kind of full nonlocality present in a hybrid functional.

1. Introduction: Local, Semilocal, and Fully Nonlocal Density Functionals

Modern electronic structure calculations for atoms, molecules, and solids are usually made within the Kohn–Sham density functional theory.^{1,2} The many-electron problem is replaced by the computationally efficient self-consistent one-electron problem, in a way that is formally exact for the ground-state energy and the electron spin densities. In

practice, some approximation must be made for the exchange–correlation energy E_{xc} as a functional of the electron spin densities $n_{\uparrow}(\vec{r})$ and $n_{\downarrow}(\vec{r})$. E_{xc} is the correction to the Hartree approximation without self-interaction correction and provides most of the binding between atoms. Its functional derivative $\delta E_{xc}/\delta n_{\sigma}(\vec{r})$ is the exchange–correlation potential seen by the fictitious noninteracting electrons.

The exact E_{xc} can be expressed^{3–5} as the electrostatic interaction between an electron at position \vec{r} and the density $n_{xc}(\vec{r}, \vec{r}')$ at \vec{r}' of the coupling constant averaged exchange–correlation hole that surrounds it:

$$E_{xc} = (1/2) \int d^3r n(\vec{r}) \int d^3r' n_{xc}(\vec{r}, \vec{r}') / |\vec{r}' - \vec{r}| \quad (1)$$

Here $n_{xc} = n_x + n_c$ is the sum of the separate exchange and correlation holes. The exchange hole density is non-

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positive and integrates over \vec{r}' to -1 and is the same as in the Hartree–Fock theory (apart from the difference between Kohn–Sham and Hartree–Fock orbitals). The correlation hole density integrates over \vec{r}' to zero. It is negative and Coulomb cusped at a small interelectronic separation $u = |\vec{r}' - \vec{r}|$ but typically positive at a large separation, where (in the system and spherical average of eq 1 that determines E_{xc}) it tends to cancel some or all of the exchange hole density. The exact exchange–correlation hole density is bounded by the electron density: $n_{xc}(\vec{r}, \vec{r}') \geq -n(\vec{r}')$.

Semilocal approximations:

$$E_{xc}^{sl}[n_t, n_i] = \int d^3r n c_{xc}^{sl}(n_t, n_i, \nabla n_t, \nabla n_i, \dots) \quad (2)$$

where $n = n_t + n_i$, are simple and computationally tractable and are sometimes usefully accurate. The local spin density approximation (LSDA),^{1,6,7} which employs only the local spin densities as arguments in eq 2, is exact for a uniform electron gas and is still often used to describe solids. The generalized gradient approximation (GGA),⁸ which adds the gradients of the local spin densities, can give a much better description of atoms and molecules, and in particular of the atomization energy of a molecule. LSDA and GGA are the first two rungs of a ladder of density functional approximations.⁹ The third or *meta*-GGA rung, which can be accurate for both molecules^{10,11} and solids¹⁰ near equilibrium, adds the spin-resolved noninteracting kinetic energy densities of the occupied orbitals, $\tau_{\sigma}(\vec{r}) = \sum_{\alpha} |\nabla \psi_{\alpha\sigma}(\vec{r})|^2 / 2$. Although the Kohn–Sham orbitals $\psi_{\alpha\sigma}$ are fully nonlocal functionals of the electron spin densities, *meta*-GGA is also semilocal in the sense that it employs only the information in an infinitesimal neighborhood of position \vec{r} , that is available in any Kohn–Sham calculation. The added arguments in eq 2 can be used to satisfy additional exact constraints, and in fact, the three semilocal rungs of the ladder have been constructed in this way without empirical parameters.^{7,8,10} Semilocal functionals require only a single integration over \vec{r} , while fully nonlocal functionals require (at least in principle) a double integration over \vec{r} and \vec{r}' .

Models for the spherically- and system-averaged hole exist for many of the semilocal functionals. In some cases, the functionals are derived from models for this hole. In other cases, the hole models are “reverse engineered”^{12,13} from the functionals. Sophisticated semilocal holes $n_{xc}^{sl}(\vec{r}, \vec{r}')$ are found to be of shorter range than the LSDA hole and are necessarily not long ranged in the separation $|\vec{r}' - \vec{r}|$, since they employ only information from an infinitesimal separation. To the extent that the exact exchange–correlation hole is also of short or intermediate range, sophisticated semilocal approximations can work well. Because the exact exchange–correlation hole is typically deeper and more short-ranged for exchange and correlation together than for exchange, semilocal functionals are typically more accurate for exchange and correlation together than for either of them separately.¹⁴ This error cancellation between semilocal exchange and correlation manifests much more strongly in the atomization energies of molecules than it does in the surface energy of jellium, where a sophisticated semilocal functional can accurately predict the separate exchange and correlation contributions.¹⁰

As argued in greater detail in ref 14, making the exchange–correlation hole density more localized around its electron leads to a lower total energy. This effect is manifested in the atomization energy of a molecule, the total energy difference between the free component atoms and the molecule, all at rest. Exact exchange without correlation underbinds chemically, underestimating the atomization energy, because the exact exchange hole in a molecule is too spread out in comparison with the exact exchange–correlation hole. LSDA overbinds molecules, overestimating the atomization energy, because it makes the holes too diffuse, more so in the free atoms than in the molecule. GGA overbinds less, producing a realistic hole localization in the free atoms but somewhat too much hole localization in the molecule or solid. Further improvement of the molecular atomization energy and the solid-state properties can be achieved by using *meta*-GGA, or using a global hybrid functional (mixing in with GGA or *meta*-GGA a little exact exchange, which yields more hole delocalization in the molecule or solid), or by using both.

To the extent that the *exact* exchange–correlation hole is long-ranged, as it can be in systems with multiple atomic centers, sophisticated semilocal functionals fail, and fully nonlocal ones are needed.¹⁴ This problem can become increasingly worse for stretched bonds and for dissociation limits,¹⁵ where it can be solved to some extent by fourth-rung functionals or hyper-GGA’s that employ information about exact exchange, such as global, local, or range-separated hybrid functionals (all of which rely on empirical parameters).¹⁴ These dissociation problems of “many-electron self-interaction freedom”¹⁵ are distinct from the problem of long-range van der Waals attraction, which is not accounted for even by the fourth-rung or hybrid functionals. Recently, Langreth, Lundqvist and their Rutgers–Chalmers collaborators have proposed a useful double-integral nonlocal functional for the van der Waals interaction¹⁶ (vdW-DF), which does not employ exact exchange and so probably does not correct the dissociation limit problems.

Fifth-rung functionals employ the unoccupied as well as the occupied Kohn–Sham orbitals in a fully nonlocal way that can potentially solve both these problems. The simplest fifth-rung functional is the random phase approximation (“in a density functional context”^{3,5,17}), as discussed in Section 2.

Yan, Perdew and Kurth¹⁸ found LSDA and GGA corrections to RPA (nearly the same in GGA as in LSDA) by taking the difference between the same semilocal functional constructed beyond and within RPA. Their corrected RPA is called RPA+. They claimed that the correction to RPA is a short- or intermediate-range effect and, thus, is well modeled at the semilocal level. That claim is correct in the uniform electron gas,^{7,12} the jellium surface,¹⁹ and the free atom.^{18,20} (In the free atom, the exact and RPA holes cannot be long-ranged.) Their corrections were accurate for the total energies of atoms (where RPA energies are too negative by about 0.02 hartree/electron, due to a too-negative on-top hole

density $n_{xc}^{\text{RPA}}(\vec{r}, \vec{r}')$.^{12,13} Jiang and Engel²⁰ found that these corrections also improve the RPA ionization energies of free atoms.

The approach of ref 18 unfortunately has no natural extension to find a *meta*-GGA for the correction to RPA, since a constraint used in the construction of the beyond RPA *meta*-GGA,¹⁰ zero correlation energy for all one-electron densities, has no analog within RPA (and another constraint on the low-density limit would require new calculations). For the one-electron density of the molecule H_2^+ , the RPA correlation energy is small for compressed and equilibrium bond lengths but is disturbingly large for long bond lengths.²¹

Reference 18 also computed the LSDA and GGA corrections to RPA atomization energies. Atomization energies were increased by typically 1 kcal/mol, suggesting that RPA would be accurate for atomization energies and that RPA+ still more so. The smallness of the computed correction is easy to understand: If the correction to RPA were +0.02 hartree/electron, then it would exactly cancel out of the atomization energy since there are as many electrons in the component free atoms as in the molecule. Puzzlingly, the careful RPA calculations of molecular atomization energies by both Furche²² and Harl and Kresse²³ found that these atomization energies were too low by typically 10 kcal/mol, in comparison to experiment. We will argue here that the correction to RPA in molecules requires full nonlocality of the kind found in fourth-rung or hybrid functionals. This correction is too long-ranged for LSDA and GGA, although it is still possible that the RPA hole is correct at a longer range. RPA is computationally much more expensive than GGA or *meta*-GGA,^{22–28} but in view of the good performance of RPA and RPA+ for solids^{24–27} and surfaces^{19,25} and of continuing improvements in RPA implementation,²⁸ it is important to find a general (hence fully nonlocal) correction. After discussing RPA in Section 2, we will mention some of the nonlocal corrections already proposed and tested.

2. The Random Phase Approximation

The roots of RPA go back to the plasma theory of electron correlation by Bohm and Pines^{29,30} in the 1950s. In those days, the focus was on the uniform electron gas, for which finite-order perturbation theory in the electron–electron interaction diverges in second order, requiring a partial resummation to all orders. The orbitals for the electron gas are just plane waves in both the Hartree and Kohn–Sham schemes, but before the Kohn–Sham theory was proposed, the Hartree orbitals would likely have been chosen even for inhomogeneous systems, where they yield unrealistic densities. The work of Langreth and Perdew^{3,5,17} brought RPA into the density functional context by introducing the Kohn–Sham orbitals for inhomogeneous systems, which depend only on the true electron density and are, therefore, independent of the coupling constant. Quantum chemists may recognize RPA as a ring coupled cluster doubles approach;³¹ a coupled cluster code can be simplified to do RPA.

The RPA is the simplest member of the family of adiabatic-connection fluctuation–dissipation theorem density functional methods.^{3–5,17,25,32,33} The Kohn–Sham nonin-

teracting system and the real interacting system are assumed to be adiabatically connected through a series of systems, all at the same electron density, in which the electron–electron interaction is $\lambda/|\vec{r}' - \vec{r}|$, where $0 \leq \lambda \leq 1$. The adiabatic-connection functionals employ exact exchange. Because they also require the unoccupied orbitals (and the orbital energies) for correlation, they stand at the top of the Jacob’s ladder⁹ of approximations, more sophisticated and more computationally demanding than lower-rung functionals. The zero-temperature fluctuation–dissipation theorem is used to express the ground-state correlation energy functional in terms of the imaginary part of the frequency-dependent density–density response function $\chi_\lambda(\vec{r}, \vec{r}'; \omega)$:

$$E_c = -\frac{1}{2} \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{\pi} \int d^3r d^3r' \text{Im}[\chi_\lambda(\vec{r}, \vec{r}'; \omega) - \chi_0(\vec{r}, \vec{r}'; \omega)] / |\vec{r}' - \vec{r}| \quad (3)$$

where $\chi_\lambda(\vec{r}, \vec{r}'; \omega)$ satisfies the Dyson equation:

$$\chi_\lambda = \chi_0 + \chi_0^* (\lambda v_{\text{Coul}} + f_{xc,\lambda})^* \chi_\lambda \quad (4)$$

$$\chi_0(\vec{r}, \vec{r}'; \omega) = \sum_{\alpha, \alpha', \sigma} \frac{\theta(\mu - \epsilon_\alpha) - \theta(\mu - \epsilon_{\alpha'})}{\omega + i0^+ + \epsilon_\alpha - \epsilon_{\alpha'}} \psi_\alpha^*(\vec{r}) \psi_{\alpha'}(\vec{r}) \psi_{\alpha'}^*(\vec{r}') \psi_\alpha(\vec{r}') \quad (5)$$

$f_{xc,\lambda}$ is the exchange–correlation kernel and is not known exactly as an explicit density functional. We can relate eqs 3 to 1 by defining:

$$n(\vec{r}) n_c(\vec{r}, \vec{r}') = - \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{\pi} \text{Im}[\chi_\lambda(\vec{r}, \vec{r}'; \omega) - \chi_0(\vec{r}, \vec{r}'; \omega)] \quad (6)$$

The simple or direct RPA we discuss here sets $f_{xc,\lambda} = 0$ (time-dependent Hartree response). (There is also a more elaborate “RPA with exchange” (RPAE), which sets $f_{xc,\lambda} = f_{x,\lambda}$ time-dependent exact-exchange-only response, so that for a one-electron density $\chi_\lambda = \chi_0$ and $E_c = 0$.) RPA becomes relatively exact for the uniform gas^{7,12} in the high-density limit. It includes a reasonable description of the long-ranged van der Waals interaction. It is even able to describe the strong static correlation in the dissociation of the H_2 molecule in a spin-restricted formalism.³⁴ The RPA correlation energy can also be expressed as the change in the zero-point energy of the plasmons or the collective density oscillations.²⁸ In many cases, RPA provides a good description of the long-range exchange–correlation hole, but it has too much short-range correlation, making a total-energy error of roughly –0.02 hartree/electron at high and normal electron densities.

The correction to RPA in the high-density limit is the second-order exchange energy. More generally, the dominant correction is a higher order exchange effect, which in finite systems provides a kind of self-interaction correction^{35,36} to RPA correlation. Thus, one might make a Perdew–Zunger³⁵ self-interaction-corrected RPA:

$$E_c^{\text{RPASIC}} = E_c^{\text{RPA}}[n_i, n_i] - \sum_{\alpha \in \text{occup}} E_c^{\text{RPA}}[n_{\alpha\sigma}, 0] \quad (7)$$

where $n_{\alpha\sigma}(\vec{r}) = |\psi_{\alpha\sigma}(\vec{r})|^2$ is the one-electron density of an occupied orbital. For the H atom, this SIC correction is +0.02 hartree (the value also predicted by the GGA correction), but for infinitely stretched H_2^+ , the SIC correction is +0.17 hartree.²¹ This fact suggests that the correction to RPA can be highly nonlocal in stretched bond situations. Of course, eq 7 is not very practical, requiring an RPA calculation for each occupied orbital density. (To satisfy the uniform-gas limit, it would be better to replace RPA by RPA+ in eq 7.)

A different fully nonlocal correction models the exchange–correlation kernel $f_{xc,\lambda}(\vec{r},\vec{r}';\omega')$.^{32,33} Another, at greater cost, is the RPAE defined above. Still another makes an RPA-based range-separated hybrid functional.^{37,38} In the range separation approach, the Coulomb interaction between electrons is smoothly divided into a short- and long-ranged part, with the help of an empirical range separation parameter. Then the long-range part of eq 1 is evaluated using RPA or related methods, while the short-range part is evaluated using a modified semilocal functional. While these various nonlocal corrections are sometimes successful, they have not provided a clear conceptual answer to the RPA atomization energy puzzle, and they are computationally demanding. We will discuss simpler corrections to RPA in the rest of this paper.

3. Additive Density Functional Correction of RPA

Yan, Perdew, and Kurth¹⁸ have presented a semilocal (sl) short-range correction to RPA correlation. Their RPA+ is

$$E_c^{\text{RPA}+}[n_\uparrow, n_\downarrow] = E_c^{\text{RPA}}[n_\uparrow, n_\downarrow] + \{E_c^{\text{sl}}[n_\uparrow, n_\downarrow] - E_c^{\text{slRPA}}[n_\uparrow, n_\downarrow]\} \quad (8)$$

The semilocal functional can be either LSDA or GGA, and there is typically little difference between these two choices. Their beyond-RPA GGA was PBE,⁸ while their within-RPA GGA was constructed by a real-space cutoff of the RPA gradient expansion for correlation, similar to the one that (beyond RPA) yields PBE.³⁹ Since RPA was expected to be exact at long-range and LSDA or GGA is accurate at short-range, RPA+ was expected to provide an accurate correction.¹⁸ RPA+ dramatically improves total energies of free atoms,¹⁸ without damaging jellium surface energies.¹⁹ More generally, RPA+ provides a useful correction to RPA in a free atom or an atomic ion, where the exchange–correlation hole and every component of it are well-localized around the electron and, thus, can be accurately described by a semilocal approximation. Numerical evidence for this can be found in the work of Jiang and Engel.²⁰ For neutral atoms (He, Li, Be, N, Ne, Mg, P, and Ar), they found that the RPA correlation energy is too negative, on average, by 0.021 hartree/electron, while the RPA+ correlation energy is too negative by only 0.002 hartree/electron. For eight free atoms and atomic ions (Li, Be⁺, Be, B⁺, Na, Mg⁺, Mg, and Al⁺), they found that the RPA first ionization energy is too large, on average, by 0.017 hartree, while the RPA+ first ionization energy is too large by only 0.002 hartree. Unfortunately, as described in Section 1, RPA+ significantly underestimates the atomization energy of a molecule, by an average of about

10 kcal/mol,^{22,23} while the PBE–GGA overestimates them by about the same amount. In one sense, this is still a good result.^{22,28} For atomization energies, RPA+ makes about the same absolute error as PBE, but without the strong error cancellation between exchange and correlation that PBE demonstrates. But greater accuracy is desired, especially since the RPA calculation is expensive.

Since a fully nonlocal correction to RPA is needed, the natural next step beyond eq 8 is

RPA++:

$$E_c^{\text{RPA}++}[n_\uparrow, n_\downarrow] = E_c^{\text{RPA}}[n_\uparrow, n_\downarrow] + \{E_c^{\text{nl}}[n_\uparrow, n_\downarrow] - E_c^{\text{nlRPA}}[n_\uparrow, n_\downarrow]\} \quad (9)$$

where nl is a fully nonlocal approximation that can be constructed both beyond and within RPA. The last requirement can only be satisfied by a nonempirical functional. If the fully nonlocal approximation happens to be a functional of the total density $n = n_\uparrow + n_\downarrow$, we define

$$E_c^{\text{RPA}++}[n_\uparrow, n_\downarrow] = E_c^{\text{RPA}+}[n_\uparrow, n_\downarrow] + \{E_c^{\text{nl}}[n] - E_c^{\text{nlRPA}}[n]\} - \{E_c^{\text{sl}}[n] - E_c^{\text{slRPA}}[n]\} \quad (10)$$

which starts from RPA+ and then corrects it for the difference between nl and sl applied to the total density. From now on, we will take the semilocal functional to be sl = GGA.

4. vdW-DF Fully Nonlocal Functional

The vdW-DF correlation energy¹⁶ is a nonempirical fully nonlocal functional of the total density:

$$E_c^{\text{vdW-DF}}[n] = E_c^{\text{LDA}}[n] + \Delta E_c^{\text{nl}}[n] \quad (11)$$

and, thus, a candidate for our eq 10. (Its variant of ref 40 is a functional of the spin densities and, thus, a candidate for our eq 9.) In eq 11, the first term is the local density approximation (LDA). The second term is a double integral over position space:

$$\Delta E_c^{\text{nl}} = (1/2) \int d^3r \int d^3r' n(\vec{r}) \varphi([n]; \vec{r}, \vec{r}') n(\vec{r}') \quad (12)$$

constructed to vanish for a uniform density and to provide a van der Waals interaction between isolated fragments of electron density. The uniform-gas correlation energy per particle appears in both terms of eq 11, and we know this quantity both beyond and within RPA,⁷ so we can use eq 11 to construct a nonempirical and fully nonlocal correction to RPA, one which is certainly correct in its LDA term. Of course, the authors of the vdW-DF never intended it to be used to find a correction to RPA.

Our RPA+ approximation of eq 8 for the correlation energy can be written as

$$\text{RPA} + = \text{RPA} + \{\text{GGAsdf}\} \quad (13)$$

where a curly bracket denotes a deviation of beyond-RPA from within-RPA correlation energy, and the argument of the curly bracket denotes the functional employed to find this deviation; for example, GGAsdf is the spin-density functional GGA. Then our RPA++ approximation of eq 10 can be written as

$$\text{RPA}++ = \text{RPA} + \{\text{sl}\} + \{\Delta\text{nl}\} \quad (14)$$

where

$$\{\text{sl}\} = \{\text{LDA}\} + \{\text{GGA}_{\text{sdf}}\} - \{\text{GGA}_{\text{df}}\} \quad (15)$$

is the semilocal part of the correction, GGA_{df} is the total-density functional GGA, and $\{\Delta\text{nl}\}$ is the fully nonlocal part of the correction:

$$\{\Delta\text{nl}\} = \Delta E_c^{\text{nl}} - \Delta E_c^{\text{nlRPA}} \quad (16)$$

where ΔE_c^{nl} is given by eq 12.

For numerical evaluation, we have taken 10 molecular atomizations from ref 22. The semilocal part of the correction, eq 15, was computed from a modified GAUSSIAN03 code,⁴¹ using a fixed accurate molecular geometry, the 6-311+G(3df,2p) basis set and a ultrafine grid. For each of the various semilocal correlation functionals, a self-consistent calculation was made with the fixed spin-density PBE–GGA exchange energy functional; this ensured that all considered electron densities for a particular atom or molecule were realistic and similar. For a given level of correlation functional (say the total-density PBE–GGA), the density difference between the within- and beyond-RPA versions was even smaller because the correlation potentials differed by a nearly constant 0.02 hartree over most of the density. Our RPA+ values from Tables 1 and 2 agree fully with those of ref 22. The fully nonlocal part of eq 14, a computationally expensive double integral, was evaluated non-self-consistently from the PBE density using a smaller grid and a special approach, as described in the Appendix.

Table 1 shows how the semilocal parts of the correction to RPA, from eq 15, contribute to the atomization energies. The individual terms in Table 1 are rather small and tend to cancel one another when combined together. Table 2 shows the RPA and experimental atomization energies from ref 22 as well as the corrected RPA+ and RPA++ atomization energies (including the fully nonlocal contribution $\{\Delta\text{nl}\}$). Our RPA++ method improves over RPA+, but neither gives significant improvement over RPA. The vdW-DF, on which our RPA++ results are based, is fully nonlocal in the way needed to describe dispersion interaction but not in the way needed to correct RPA atomization energies.

Table 1. Semilocal Contributions of Eq 15 to the RPA++ Correction to the RPA Atomization Energy, in kcal/mol, and the Total Semilocal Contribution^a

molecule	{LDA}	{GGA _{sdf} }	{GGA _{df} }	{sl} ^b
H ₂	−1.2	1.1	−1.6	1.5
N ₂	−1.9	0.1	−2.8	0.9
O ₂	−1.4	−1.2	−2.2	−0.4
F ₂	−0.8	−1.4	−1.6	−0.6
Si ₂	−1.0	0.2	−1.7	0.9
CO	−2.0	−1.4	−2.8	−0.6
CO ₂	−3.8	−3.6	−5.5	−1.9
H ₂ O	−2.6	−0.7	−3.9	0.5
C ₂ H ₂	−4.5	−2.3	−6.6	−0.2
HF	−1.4	−0.6	−2.0	0.1

^a (1 hartree = 627.5 kcal/mol). ^b {sl} = {LDA} + {GGA_{sdf}} − {GGA_{df}}.

Table 2. Ground-State Atomization Energies from RPA (ref 22), RPA+, and RPA++ Compared to the Experimental Results from Ref 22^a

molecule	RPA	RPA+	RPA++	(PBE + RPA+)/2	expt
H ₂	109	110	110	108	109
N ₂	223	223	225	234	228
O ₂	113	111	113	128	121
F ₂	30	29	30	41	38
Si ₂	70	70	71	76	75
CO	244	242	244	266	259
CO ₂	364	360	364	388	389
H ₂ O	223	222	224	228	232
C ₂ H ₂	381	378	381	397	405
HF	133	132	133	137	141
ME	−11	−12	−10	−1	
MAE	11	12	10	4	

^a Both the calculated and corrected experimental values are for static nuclei. All calculations, including RPA, use PBE orbitals. RPA+ is the GGA correction of eqs 8 and 13. RPA++ is the vdW-DF-based correction of eqs 10 and 14 with its nonlocal term $\{\Delta\text{nl}\}$ evaluated on a cubic grid (roughly 60 × 60 × 60) and with a spacing of roughly 0.17 bohr. We also show the empirical hybrid of eq 17, which averages the PBE and RPA+ exchange–correlation energies. All results are shown in kcal/mol. ME is the mean error, and MAE is the mean absolute error.

5. Global Hybrid Functional for Corrected RPA Atomization Energies

Correction of RPA atomization energies requires full non-locality but (as can be seen from Table 2) not the full nonlocality responsible for the van der Waals interaction. The other familiar kind of nonlocality is that of the global, local, and range-separated hybrids.^{14,37,38} We have found empirically that the global hybrid of 50% RPA+ with 50% PBE–GGA:

$$E_{\text{xc}}^{\text{hyb}} = (1/2)[E_{\text{xc}}^{\text{RPA}+} + E_{\text{xc}}^{\text{PBE-GGA}}] = E_{\text{xc}}^{\text{RPA}+} + 0.5[E_{\text{xc}}^{\text{PBE-GGA}} - E_{\text{xc}}^{\text{RPA}+}] \quad (17)$$

i.e.:

$$E_c^{\text{hyb}} = E_c^{\text{RPA}+} + 0.5[E_{\text{xc}}^{\text{PBE-GGA}} - E_{\text{xc}}^{\text{RPA}+}] \quad (18)$$

yields accurate atomization energies, as shown in Table 2. Equation 18 is exact for the uniform or slowly varying electron gas, but its empirical construction makes it somewhat unsatisfactory as a general correction to RPA. Moreover, it shares with other global hybrids the defect that its correlation energy for an inhomogeneous system scales improperly, like exchange in the high-density limit.⁴² However, it does suggest the physics that a proper correction must have: RPA+ atomization energies are too low because the RPA+ exchange–correlation hole is too spread out in a molecule. The PBE–GGA atomization energies are too high because the PBE–GGA exchange–correlation hole is not spread out enough in a molecule. The hybrid of eq 17 achieves about the right spread of the exchange–correlation hole in a molecule.

Our global hybrid of RPA+ with PBE differs in detail from the more standard global hybrids of GGA or *meta*-GGA with a fraction of exact exchange. GGA's or *meta*-GGA's tend to be the most accurate near the upper or

Table 3. Jellium Surface Exchange–Correlation Energies σ_{xc} in erg/cm². The bulk density is $n = 3/(4\pi r_s^3)$, with r_s in bohr^a

r_s	LDA	RPA	RPA+	ISTLS	(PBE + RPA+)/2
2.00	3354	3467	3413	3417	3337
2.07	2961	3064	3015	3026	2948
2.30	2019	2098	2060	2072	2011
2.66	1188	1240	1214	1227	1183
3.00	764	801	781	800	761
3.28	549	579	563	580	547
4.00	261	278	268	(281)	260
6.00	53	58	54	(60.5)	53

^a The electron density at the surface is more slowly varying for smaller r_s . All calculations, including RPA, use LDA orbitals. The exact surface exchange–correlation energy probably (ref 19) falls in the narrow range between LDA and RPA. RPA and ISTLS values from ref 19 are compared to LDA and RPA+ values from ref 18. While RPA+ makes a GGA correction to RPA, ISTLS makes a promising fully nonlocal correction. The last column is from our global hybrid of eq 17. Note that the exchange–correlation contribution can far exceed the total surface energy.

physical limit of the coupling constant integration³ and the least accurate at the lower limit, where exchange dominates. But RPA+ is actually exact at the lower limit and makes its greatest error near the upper limit.

Reference 38 presents two range-separated hybrids that use a RPA or scaled RPA exchange–correlation hole at long-range and a LSDA hole at short-range. One of the authors (B. Janesko) of ref 38 kindly provided us with the errors for our 10 molecules. The MAEs are 5.8, 4.2, and 4.2 kcal/mol for their one- and two-parameters and for our one-parameter hybrids, respectively. Range-separated hybrids might achieve higher accuracy through the replacement of LSDA by GGA or *meta*-GGA holes.

In Table 3, we test the global hybrid of eqs 17 and 18 for the jellium surface energy. While the exact surface exchange–correlation energy is unknown, it probably¹⁹ falls in the narrow range between LDA and RPA. Our global hybrid values fall at or a little below the lower end of this range (while PBE–GGA falls well below).

6. Conclusions

The random phase approximation (RPA) is a promising^{18–20,22–28,34} fifth-rung density functional, but one that requires a correction. The correction to the total^{18,20} and the ionization²⁰ energies of a free atom, or to the surface energy of a solid,^{19,25} is a short-range correlation describable by LSDA or GGA (RPA+), but RPA molecular atomization

energies^{22,23} surprisingly require a fully nonlocal correction, which we argue arises due to the multiple atomic centers of the molecule. The nonlocal RPA++ correction, based upon the vdW-DF,¹⁶ is, however, not very different from RPA+. (And probably the vdW-DF correlation functional, like the LSDA and the GGA, does not have the kind of nonlocality that would make it compatible with exact exchange for molecular atomization energies.) The needed kind of nonlocality is present instead in the global hybrid functional of eq 17. The RPA, RPA+, and RPA++ exchange–correlation holes in a molecule can be more localized around an electron than that of the exact exchange hole but still too spread out in comparison to the exact exchange–correlation hole. While the global hybrid of eq 17 is not a satisfactory general correction to RPA, its accuracy strongly suggests this conclusion. RPA may still be nearly correct at longer range in normal systems, justifying range-separated hybrids, such as refs 37 and 38. However, the range-separated hybrids share two drawbacks with the global hybrids: the appearance of an empirical parameter and the incorrect behavior under uniform density-scaling to the high-density limit.^{43,42}

A satisfactory fully nonlocal correction should be constructed by constraint satisfaction, without empirical parameters. A nonempirical self-interaction correction to RPA correlation is intrinsic to the inhomogeneous Singwi–Tosi–Land–Sjoelander (ISTLS) functional.^{44,19} ISTLS is nearly exact for the uniform electron gas and yields jellium surface energies close to those of RPA+ (Table 3). So it would be interesting to see what ISTLS predicts for molecular atomization energies. Equally interesting would be atomization energy and surface energy tests of the “RPA with exchange”, as defined in Section 2, with a small LSDA additive correction (RPAE+). RPAE already shows promise for the correlation energies of atoms.⁴⁵ References 19 and 46 suggest that, while the spatial dependence of $f_{x,\lambda}(\vec{r},\vec{r}';\omega)$ might be important, the frequency dependence might not be. The fully nonlocal second-order screened exchange correction to RPA, related to RPAE, has been used recently by Grueneis et al.⁴⁷

7. Appendix

Numerical Double Integration on a Three-Dimensional Grid. Semilocal functionals (eq 2) require only a single integration over a three-dimensional grid of M points, with a computation time proportional to M . Fully nonlocal functionals require a double integration, with a computation time proportional to M^2 . Thus, grids commonly used for

Table A1. Contribution of the Beyond-RPA vdW-DF Nonlocal Energy ΔE_c^{nl} (Hartree) of Eq 12 to the Atomization Energy of the N₂ Molecule vs the Spacing of the Grid Points (Bohr)^a

spacing of the grid points	nonlocal contribution	core elimination	gradient calculation
0.237–0.224	0.01528	no	numeric
0.197–0.186	0.01227	no	numeric
0.168–0.159	0.01063	no	numeric
0.200	0.01343	no	analytic
0.200	0.01151	yes	numeric
0.200	0.01192	yes	analytic
0.150	0.01083	yes	analytic

^a The effect of making the same core elimination for free atoms and molecules is shown in the last three lines. Where two spacings are given on one line, the first is for the molecule, and the second is for the free atom.

Table A2. Convergence of $\{\Delta n\} = \Delta E_c^{\text{nl}} - \Delta E_c^{\text{IPRA}}$ (Hartree) vs the Spacing of the Grid Points (Bohr)^a

system	spacing of the grid points	nonlocal correction	core elimination	gradient calculation	atomization
N ₂	0.237	0.01231	no	numeric	1.15
N ₂	0.197	0.01257	no	numeric	1.00
N ₂	0.168	0.01268	no	numeric	0.92
N ₂	0.200	0.01249	no	numeric	1.00
N ₂	0.200	0.01280	yes	numeric	0.95
N ₂	0.200	0.01310	no	analytic	0.98
N ₂	0.200	0.01309	yes	analytic	0.98
N ₂	0.150	0.01329	yes	analytic	0.96
N	0.224	0.00707	no	numeric	
N	0.186	0.00708	no	numeric	
N	0.159	0.00707	no	numeric	
N	0.200	0.00704	no	numeric	
N	0.200	0.00716	yes	numeric	
N	0.200	0.00732	no	analytic	
N	0.200	0.00733	yes	analytic	
N	0.150	0.00741	yes	analytic	

^a ΔE_c^{nl} is the nonlocal expression of eq 12. The last column shows the contribution (kcal/mol) of $\{\Delta n\}$ to the N₂ atomization energy. For example, for spacing = 0.0150 bohr, with core elimination and analytic gradients, this is $2(0.00741) - 0.01329$ hartree = 0.00153 hartree = 0.96 kcal/mol.

semilocal functionals can be impractical for fully nonlocal ones. For the contributions of $\{\Delta n\}$ to the RPA++ atomization energies of Table 2, we used cubic grids (roughly $60 \times 60 \times 60$) with spacings of roughly 0.17 bohr. The grids for the molecule and the free atom were slightly different. The high-density cores were eliminated, somewhat as in the pseudopotential approach usually employed with the vdW-DF: Where $n > 1$ ($r_s < 0.6$), we set $n = 1$ and $\nabla n = 0$. With this core elimination, we can achieve a given level of convergence with a coarser grid, as shown in Table A1.

Later we devised the more elaborate methods described below, which confirmed our earlier result of Table 2 for N₂ and C₂H₂, and could be used for future work. These methods take maximum advantage of the error cancellation between molecule and free atoms. (We have not attempted to use the efficient implementation of the vdW-DF presented in ref 48).

For dissociation energy calculations of diatomic molecules, we use a cubic grid centered on the bond critical point of the molecule. This grid is typically displaced with respect to the atomic nuclei. The same displacement and density grid were used for the free atom. This way the electron density and its gradient are directly comparable for free atoms and molecules; the grid points have exactly the same arrangement around the nucleus.

In our calculations of Table 2, the density gradients were evaluated numerically on the grid. In Tables A1 and A2, we also check the effect of using analytic gradients instead of numerical ones.

Tables A1 and A2 show that, while the nonlocal contribution to the beyond-RPA correlation energy and the nonlocal correction to the RPA correlation energy are not so well converged, the nonlocal correction to RPA atomization energies is well converged.

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