Beyond the RPA on the cheap: improved correlation energies with the efficient “Radial Exchange Hole” kernel

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The “ACFD-RPA” correlation energy functional has been widely applied to a variety of systems to successfully predict energy differences, and less successfully predict absolute correlation energies. Here we present a parameter-free exchange-correlation kernel that systematically improves absolute correlation energies, while maintaining most of the good numerical properties that make the ACFD-RPA numerically tractable. The “RXH” kernel is constructed to approximate the true exchange kernel via a carefully weighted, easily computable radial averaging. Correlation energy errors of atoms with two to eighteen electrons show a thirteenfold improvement over the RPA and a threefold improvement over the related “PGG” kernel, for a mean absolute error of 13mHa or 5%. The average error is small compared to all but the most difficult to evaluate kernels. van der Waals C_6 coefficients are less well predicted, but still show improvements on the RPA, especially for highly polarisable Li and Na.

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Standard groundstate DFT methods¹ under local density functional approaches such as the LDA, GGA or exact exchange (EXX)² approach have long been a fundamental part of computational physics and chemistry. However, these functionals fail to reproduce important van der Waals (vdW) dispersion physics.³ With increasing computer resources, the ACFD-RPA functional approach, recently reviewed in Eshuis, Bates and Furche⁴ (EBF) and Ren *et al.*,⁵ has proved to be a versatile and fairly efficient^{6–12} means of evaluating correlation energies, albeit one that typically overpredicts absolute correlation energies due to its neglect of physics found in the exchange-correlation kernel f^{xc} .

The ACFD-RPA is typically employed as a “post groundstate” method, where a groundstate Kohn-Sham (KS) potential¹ is generated self-consistently in a standard approach (eg. the LDA or EXX) and the orbitals are then used to refine the exchange-correlation energy without further self-consistency. Here the bare response function $\chi_0(\mathbf{x}, \mathbf{x}'; i\omega)$ is evaluated e.g. from the occupied and unoccupied orbitals of a groundstate KS system and used to evaluate the interacting response via

$$\chi_\lambda = \chi_0 + \chi_0 \star w_\lambda \star \chi_\lambda \quad (1)$$

where $\star$ represents an integral/sum over $\mathbf{x} \equiv \mathbf{r}\sigma$. The effective interaction term w_λ takes the form

$$w_\lambda(\mathbf{x}, \mathbf{x}'; i\omega) \equiv v_\lambda^C(|\mathbf{r} - \mathbf{r}'|) + f_\lambda^{\text{xc}}(\mathbf{x}, \mathbf{x}'; i\omega) \quad (2)$$

where $v_\lambda^C(R) = \lambda/R$ is a Coulomb potential and f_λ^{xc} is the exchange-correlation kernel. Often $f_\lambda^{\text{xc}}(\mathbf{x}, \mathbf{x}'; i\omega)$ is replaced by its zero frequency expression

$$f_\lambda^{\text{xc}}(\mathbf{x}, \mathbf{x}'; 0) = \frac{\delta V_\lambda^{\text{xc}}(\mathbf{x})}{\delta n(\mathbf{x}')} \equiv \frac{\delta^2 E_\lambda^{\text{xc}}}{\delta n(\mathbf{x})\delta n(\mathbf{x}')}, \quad (3)$$

or set to zero under the random-phase approximation (RPA). Finally the correlation energy can be evaluated

through the so-called “ACFD” functional (see Section 2.1 of EBF⁴ for details)

$$E^c = -\frac{1}{2} \int_0^1 d\lambda \int_0^\infty \frac{d\omega}{\pi} \text{Tr} [(\chi_\lambda - \chi_0) \star v_1^C]. \quad (4)$$

This is then combined with the KS kinetic energy T^{KS} , external energy E^{Ext} and Hartree and exchange energy E^{Hx} to produce the electronic groundstate energy

$$E_0 = T^{\text{KS}} + E^{\text{Ext}} + E^{\text{Hx}} + E^c. \quad (5)$$

By neglecting the exchange-correlation kernel f^{xc} , the RPA has some considerable numerical advantages that are often exploited [see eg. Section 3 of EBF,⁴ Ref. 13 and Ref. 5] to make calculations numerically efficient. However, while the ACFD-RPA often predicts good energy differences, it is quite poor at predicting absolute correlation energies, especially in small atoms and molecules¹⁴ where it can overpredict correlation energies by as much as 150%. These inaccuracies come from failures in the short-range physics of interactions, arising from neglect of the f^{xc} kernel. For example the opposite-spin pair-density $n_{2\sigma\neq\sigma'}(\mathbf{r}, \mathbf{r}')$ arising from the RPA can be negative for $\mathbf{r} \approx \mathbf{r}'$, a physically implausible result that in turn contributes to overestimation of the absolute correlation energy. When taking energy differences these short-range errors tend to cancel each other out, which explains the RPA’s success for these calculations.

Various approximations to f^{xc} , and other means to correct RPA absolute energies have been proposed and can be broadly divided into additive methods^{14,15} that do not much affect dispersion interactions³ and kernel methods^{13,16–24} that do. The most successful (and most numerically difficult) for atoms and molecules is the tdEXX^{21,22} functional. Here the exact exchange kernel f^{x} is used to produce very accurate correlation energies, suggesting that the exchange kernel is sufficient for all but the most intractable problems. Indeed many

techniques^{13,14,19–22} base their corrections on exchange alone.

Much of the numerical advantage of the RPA comes from the fact that w_λ is: i) linear in λ , ii) frequency independent, and iii) a function of $|\mathbf{r} - \mathbf{r}'|$ only. This allows one to perform the integration over λ analytically, the integration over frequency efficiently, and, perhaps most importantly, reduce the complexity of convolutions (*) involving w_λ by transforming to reciprocal space. For kernels with these three properties we can write the correlation energy as (in Hartree atomic units, used throughout this manuscript)

$$E^c = - \int_0^\infty \frac{d\omega}{\pi} \text{Tr} \left[\left\{ \log(\hat{1} + \hat{\chi}_0 \hat{w}_1) - \hat{\chi}_0 \hat{w}_1 \right\} \frac{\hat{v}_1}{\hat{w}_1} \right] \quad (6)$$

where $\hat{\chi}_0(\mathbf{q}, \mathbf{q}'; i\omega)$ is a two-point function in $\mathbf{q}$ and $\mathbf{q}'$ while $\hat{w}_1(\mathbf{q}, \mathbf{q}') = w_1(\mathbf{q})\delta(\mathbf{q} - \mathbf{q}')$ and $\frac{\hat{v}_1}{\hat{w}_1}(\mathbf{q}, \mathbf{q}') = \frac{v_1(\mathbf{q})}{w_1(\mathbf{q})}\delta(\mathbf{q} - \mathbf{q}')$ are diagonal one-point functions. Clearly $w_1(\mathbf{q}) = v_1(\mathbf{q}) = \frac{4\pi}{q^2}$ in the RPA, but provided f_1^{xc} is a function of $|\mathbf{r} - \mathbf{r}'|$ only, both $\hat{w}_1$ and $\hat{v}_1/\hat{w}_1$ are diagonal and (6) can be efficiently evaluated. Most approximations to the true kernel cannot be written in this form, making routine application of kernel physics difficult. The ‘‘Radial Exchange Hole’’ (RXH) kernel we shall develop in this manuscript aims to maintain these good numerical properties, while reproducing some good exchange kernel physics.

An exchange kernel of intermediate accuracy and complexity is that proposed by Petersilka, Gossmann and Gross (PGG).²⁰ They suggest approximating the exchange kernel f^x via the approach used by Krieger, Li and Iafrate²⁵ for the optimised exchange potential. One can quickly ‘derive’ their kernel by first writing the Hartree and exchange energy as $E^{\text{Hx}} = \int \frac{d\mathbf{x}d\mathbf{x}'}{2|\mathbf{r} - \mathbf{r}'|} g_{\text{Hx}}(\mathbf{x}, \mathbf{x}') n(\mathbf{x}) n(\mathbf{x}')$, where g_{Hx} is the Hartree-exchange (Hx) pair-factor defined via the groundstate Hartree and exchange pair-density n_{Hx} through $g_{\text{Hx}}(\mathbf{x}, \mathbf{x}') n(\mathbf{x}) n(\mathbf{x}') = n_{\text{Hx}}(\mathbf{x}, \mathbf{x}')$. By assuming $\delta g_{\text{Hx}}/\delta n \approx 0$ when evaluating $f_1^{\text{xc}}(\mathbf{x}, \mathbf{x}') = \delta^2 E^{\text{Hx}}/[\delta n(\mathbf{x})\delta n(\mathbf{x}')] - v_1^C$, one obtains the PGG kernel in the form $f_\lambda^{\text{xc}}(\mathbf{x}, \mathbf{x}') = \lambda[g_{\text{Hx}}(\mathbf{x}, \mathbf{x}') - 1]/|\mathbf{r} - \mathbf{r}'|$ where $g_x = [g_{\text{Hx}} - 1] < 0$ is the exchange hole pair-factor. This kernel has a number of good short-ranged properties coming from the use of the exchange hole g_x . Notably it fully cancels the same spin Coulomb interaction for $\mathbf{r} = \mathbf{r}'$, and re-introduces it quadratically for small $\mathbf{r} - \mathbf{r}'$. For H and He the kernel reproduces the true $f^x = -\delta_{\sigma\sigma'} v^C$ and spurious self-interaction is completely avoided.

We now use an approximation similar to that of PGG to produce the more efficient RXH kernel. Here we aim to reproduce the good short-range physics of the PGG kernel, while replacing the two-point behaviour of g_{Hx} by a simpler dependence on the distance $|\mathbf{r} - \mathbf{r}'|$ only. We choose²⁶ a two parameter, ‘‘radial’’ model pair-factor

g of the form

$$g(\mathbf{x}, \mathbf{x}') \equiv g_{\sigma\sigma'}(R) = \frac{c_{\sigma\sigma'} R^2 + (k_{\sigma\sigma'} R)^4}{1 + (k_{\sigma\sigma'} R)^2 + (k_{\sigma\sigma'} R)^4} \quad (7)$$

where $R = |\mathbf{r} - \mathbf{r}'|$ and the two parameters control the on-top curvature (c) and the range of the kernel (k). Clearly $g(R \rightarrow 0) = c_{\sigma\sigma'} R^2$ and $g(R \rightarrow \infty) = 1$ as desired (except for H and He where $c = k = 0$ correctly makes $g_{\sigma\sigma} = 0$ everywhere). The total interaction $w_\lambda = v_\lambda^C + f_\lambda^{\text{xc}}$ takes the desirable form

$$w_\lambda(\mathbf{x}, \mathbf{x}') = \lambda \frac{g_{\sigma\sigma'}(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \quad (8)$$

We now introduce some ‘‘exchange hole’’ constraints to the model kernel. Rather than allowing the parameters $c_{\sigma\sigma'}$ and $k_{\sigma\sigma'}$ to be freely chosen, we instead ensure that the kernel has some integrated properties of the true pair-factor. Specifically we ensure that, for each spin pair $\sigma\sigma'$, the Hx pair number and groundstate Hx energy are reproduced via

$$\int d\mathbf{r} d\mathbf{r}' [g(\mathbf{x}, \mathbf{x}') n(\mathbf{x}) n(\mathbf{x}') - n_{\text{Hx}}(\mathbf{x}, \mathbf{x}')] = 0, \quad (9)$$

$$\int \frac{d\mathbf{r} d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} [g(\mathbf{x}, \mathbf{x}') n(\mathbf{x}) n(\mathbf{x}') - n_{\text{Hx}}(\mathbf{x}, \mathbf{x}')] = 0. \quad (10)$$

The second constraint means that the ‘derivation’ of the PGG kernel given previously (where we assumed $\delta g/\delta n \approx 0$ in $\delta^2 E^{\text{Hx}}/[\delta n \delta n]$) can be made for the RXH, since $E^{\text{Hx}} = \int \frac{d\mathbf{x}d\mathbf{x}'}{2|\mathbf{r} - \mathbf{r}'|} n n' g_{\text{Hx}} = \int \frac{d\mathbf{x}d\mathbf{x}'}{2|\mathbf{r} - \mathbf{r}'|} n n' g$. The kernel might thus be considered a weighted radial averaging of the PGG kernel

The integrals give the model pair-factor g some of the same physics as the true pair-factor g_{Hx} . In particular they ensure that the dominant contribution from the kernel is short-ranged, with long-ranged effects only being felt in regions where the density (and thus response) is almost zero. This in turn helps the RXH make its most important changes to the correlation physics in regions with greatest contribution to the energy. Clearly the RXH kernel behaves quite differently to the the PGG kernel away from $\mathbf{r} = \mathbf{r}'$. For example, for electrons in different s shells (as in Li or Be) the PGG kernel g_{Hx} depends only on $|\mathbf{r}|$ and $|\mathbf{r}'|$ and is exactly zero whenever $|\mathbf{r}| = |\mathbf{r}'|$, while the RXH g depends on $|\mathbf{r} - \mathbf{r}'|$ and is non-zero for electrons with $|\mathbf{r}| = |\mathbf{r}'|$ but $\mathbf{r} \neq \mathbf{r}'$. However, if the effect of these differences on the correlation energy act in similar regions to those that dominate the exchange energy, the integral conditions (9) and (10) should ensure that the effect on the correlation energy is minimal. In fact, as results later show, the RXH kernel appears to better reproduce the true short-range physics of f^{xc} than the PGG kernel, a somewhat surprising result.

To test the RXH kernel, we apply it to atoms with two to eighteen electrons (He to Ar), using exact exchange groundstates calculations. Here we evaluate the ground-state properties under the LEXX²⁷ approximation to allow for spherically symmetric and spin homogeneous

densities. We use the same all-electron code previously employed to evaluate ISTLS correlation energies²³ with groundstate optimised effective potential approximated by the method of Krieger, Li and Iafrate²⁵ (KLI). The code is modified to reproduce the correct Hartree and exchange physics of ensembles via the method outlined in Ref. 27. We are thus able to reproduce groundstate properties, and in particular $n_{2\text{Hx}}$, accurately for both closed and open shell systems.

The linear-response calculation of χ_0 involves utilising expansions on the spherical harmonics to produce coupled functions of radial coordinates $r = |\mathbf{r}|$ and $r' = |\mathbf{r}'|$ only. To generate χ_0 we avoid sums over unoccupied orbitals and instead use Greens functions generated via a shooting method with errors coming only from the finite radial grid with $N_r < 400$ points. Energies were converged to under 1mHa or within 0.5% (whichever is the larger). Given the simple radial geometry we do not transform integrals to reciprocal space, and the RPA, PGG and RXH methods all take the same $O(N_r^3)$ time.

The parameters $c_{\sigma\sigma'}$ and $k_{\sigma\sigma'}$ of the RXH kernel (7) are evaluated by employing the secant method. Here, for a given k , we find c via (9), and k is then iterated to satisfy (10). Typically no more than ten iterations are required to accurately calculate k , although care must be taken to ensure convergence. Some example parameters ($c_{\sigma\sigma}/k_{\sigma\sigma}$) are: Be) $c = 0.127$, $k = 0.732$, O) $c = 0.667$, $k = 2.635$, Na) $c = 2.313$, $k = 3.475$, Si) $c = 4.583$, $k = 4.744$, and Ar) $c = 11.241$, $k = 5.692$.

TABLE I. Correlation energies in -mHa under the RPA, PGG and RXH approximations. Numbers in brackets are % errors. Groundstates are calculated in the LEXX approximation.

System	Exact	RPA	%	PGG	%	RXH	%
He	42	84	(100)	45	(7)	45	(7)
Li	45	113	(151)	50	(11)	50	(11)
Be	94	181	(93)	104	(11)	106	(12)
B	125	224	(79)	112	(-10)	128	(3)
C	156	277	(78)	124	(-21)	155	(-1)
N	188	337	(79)	139	(-26)	175	(-7)
O	258	406	(57)	206	(-20)	243	(-6)
F	324	491	(52)	270	(-17)	304	(-6)
Ne	390	586	(50)	332	(-15)	369	(-5)
Na	396	611	(54)	332	(-16)	379	(-4)
Mg	438	674	(54)	375	(-14)	436	(-0)
Al	470	715	(52)	385	(-18)	467	(-1)
Si	505	772	(53)	401	(-21)	506	(0)
P	540	839	(55)	419	(-22)	552	(2)
S	605	903	(49)	474	(-22)	621	(3)
Cl	666	982	(47)	527	(-21)	694	(4)
Ar	722	1072	(48)	579	(-20)	773	(7)
MAE(%)		194	(68)	66	(17)	13	(5)

^a From Ref. 28

Absolute correlation energies $-E^c$ for the atoms are

shown in Table I under the RPA, PGG and RXH approximations. It is immediately clear that, with the exception of Be, the RXH outperforms not only the RPA as expected, but also the PGG kernel. Here the mean absolute error of E^c is reduced from 194mHa for the RPA and 66mHa for the PGG down to 13mHa for the RXH. Absolute percentage errors are reduced somewhat less, but even here RXH offers a threefold improvement from 17% to 5% over the PGG kernel. For atoms with highest occupied orbitals in a p shell, the improvement is even greater still, with correlation energies approaching chemical accuracy.

It is clear that the RXH must offer an unexpected improvement over the PGG in the regions that dominate correlation energy calculations. It is likely that the spherical averaged form and integrated constraints correctly confine the kernel to be shorter-ranged than the PGG kernel. The dynamic physics will thus be reproduced better near the crucial “on-top” region. In the case of the transitions from p to s that dominate correlation energies for outermost p shells the RXH kernel significantly outperforms the PGG kernel, adding further weight to the assumption that it is the short range physics that are most important. It would be very useful to compare the exact exchange kernel f^x of Ne from a tdEXX calculation^{21,22} with its RXH kernel.

TABLE II. Same-species C_6 coefficients (Haa₀⁶) for spherical atoms in the RPA, PGG and RXH approximations.

	He	Li	Be	Ne	Na	Mg	Ar
Exact ^a	1.44	1380	219	6.48	1470	630	63.6
RPA	1.17	500	179	4.98	744	481	54.7
PGG	1.38	1340	277	5.98	1710	743	76.0
RXH	1.38	1080	231	5.19	1050	487	55.2

^a From lower bounds of Ref. 29

We have so far demonstrated that the RXH kernel is good at reproducing the intra-species correlations that feed into the correlation energy. To test its ability to predict inter-species correlations we also use the RXH kernel to evaluate van der Waals C_6 coefficients for same-species pairs. These are notoriously difficult to reproduce accurately under standard DFT or ACFD type approaches. Here the correlation energy difference of two atoms at a great distance D obeys $E^{\text{vdW}}(D) = E^c(D) - E^c(\infty) = -\frac{C_6}{D^6}$. We calculate C_6 through the Casimir-Polder formula

$$C_6 = \frac{3}{\pi} \int d\omega A(i\omega)^2, \quad (11)$$

where $A(i\omega) = \int d\mathbf{x} d\mathbf{x}' z z' \chi_1(\mathbf{x}, \mathbf{x}')$ is the dipole polarisability of a single atom.

As shown in Table II the results are mixed, with the RXH kernel being only slightly more accurate than the RPA for the large Mg and Ar atoms, but otherwise outperforming it. Importantly it greatly improves on the

RPA for Li and Na, the systems with the greatest, and thus most dominant vdW C_6 coefficients. We note that the evaluation of C_6 coefficients is quite susceptible to even minor numerical issues and small variations in the groundstate orbitals, and these results may need to be better converged and tested for a comprehensive understanding.

In summary, we have produced a “Radial Exchange Hole” (RXH) exchange-correlation kernel that is both efficient to calculate, and systematically improves on the RPA, at least for the atomic systems tested here. The kernel is derived from a similar approximation to that of PGG and is designed to model the exchange kernel $f^x(\mathbf{r}, \mathbf{r}')$ via a simple dependence on $|\mathbf{r} - \mathbf{r}'|$ only. By writing the kernel in the form (7), constrained by (9) and (10) we are able to produce a kernel that is simple and parameter free.

The RXH kernel offers improved correlation energies on all tested atoms (He to Ar) when compared with both the RPA and related PGG kernel (with the exception of Be). The mean absolute error of the atomic correlation energies is reduced to 13mHa (5%) from 66mHa (17%) and 194mHa (68%) respectively for the PGG and RPA kernels. Here the energy is dominated by the short-range physics correctly modelled by the RXH kernel. Results for vdW C_6 coefficients are more mixed, with predictions only slightly better than the RPA for Mg and Ar, but significantly better for Li, Be and Na. It is likely that longer-ranged kernel physics are involved in these calculations, and these are more poorly predicted by the RXH approximation.

While the RXH approximation derived and demonstrated here clearly performs well for correlation energies of atoms, its immediate application to molecules and atoms may prove problematic. In particular the dissociation limit of different atoms will involve finding a pair factor g through (7) that is appropriate for both atoms. This problem could be remedied by treating the kernel as a sum over localised radial pair-factors [e.g. $f^{\text{xc}} = \sum_{\mathcal{S}} \Theta_{\mathcal{S}}(\mathbf{r}) \Theta_{\mathcal{S}}(\mathbf{r}') \frac{g_{\mathcal{S}}(\mathbf{x}, \mathbf{x}') - 1}{|\mathbf{r} - \mathbf{r}'|}$ with $\Theta_{\mathcal{S}}(\mathbf{r} \notin \mathcal{S}) = 0$ for given regions $\mathcal{S}$], which we will explore in future work. Similarly in bulks, the form of the model (7) of the pair-factor is inappropriate, and an alternative approximation must be found.

Overall, however, the RXH clearly represents an approximation that is both numerically efficient, and more accurate than the RPA. Somewhat surprisingly it produces more accurate correlation energies than the related PGG approximation, and many other approximations to f^{xc} . It is clear that constraining the kernel by its integrated properties allows it to accurately reproduce the important short-ranged physics that the RPA neglects, and this is likely to apply to other expressions for g . It should thus be possible to further refine the form of the kernel, perhaps via the addition of free parameters or a similar approach to include the correlation kernel, to

improve both correlation energies and C_6 coefficients.

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- ¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140** (1965).
- ²R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953); J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
- ³J. F. Dobson and T. Gould, Journal of Physics: Condensed Matter **24**, 073201 (2012).
- ⁴H. Eshuis, J. Bates, and F. Furche, Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta) **131**, 1 (2012), 10.1007/s00214-011-1084-8.
- ⁵X. Ren, P. Rinke, C. Joas, and M. Scheffler, Journal of Materials Science, **1** (2012), 10.1007/s10853-012-6570-4.
- ⁶J. F. Dobson and J. Wang, Phys. Rev. Lett. **82**, 2123 (1999).
- ⁷F. Furche, Phys. Rev. B **64**, 195120 (2001).
- ⁸T. Miyake, F. Aryasetiawan, T. Kotani, M. van Schilfgaarde, M. Usuda, and K. Terakura, Phys. Rev. B **66**, 245103 (2002).
- ⁹M. Fuchs and X. Gonze, Phys. Rev. B **65**, 235109 (2002).
- ¹⁰J. Harl and G. Kresse, Phys. Rev. B **77**, 045136 (2008); Phys. Rev. Lett. **103**, 056401 (2009); J. Harl, L. Schimka, and G. Kresse, Phys. Rev. B **81**, 115126 (2010).
- ¹¹S. Lebègue, J. Harl, T. Gould, J. G. Ángyán, G. Kresse, and J. F. Dobson, Phys. Rev. Lett. **105**, 196401 (2010).
- ¹²L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nat Mater **9**, 741 (2010).
- ¹³A. Grüneis, M. Marsman, J. Harl, L. Schimka, and G. Kresse, The Journal of Chemical Physics **131**, 154115 (2009).
- ¹⁴H. Jiang and E. Engel, The Journal of Chemical Physics **127**, 184108 (2007).
- ¹⁵S. Kurth and J. P. Perdew, Phys. Rev. B **59**, 10461 (1999).
- ¹⁶A. Zangwill and P. Soven, Phys. Rev. Lett. **45**, 204 (1980).
- ¹⁷J. F. Dobson and J. Wang, Phys. Rev. B **62**, 10038 (2000).
- ¹⁸A. Savin and H.-J. Flad, International Journal of Quantum Chemistry **56**, 327 (1995); J. Toulouse, A. Savin, and H.-J. Flad, Int. J. Quantum Chem. **100**, 1047 (2004); J. Toulouse, W. Zhu, J. G. Ángyán, and A. Savin, Phys. Rev. A **82**, 032502 (2010).
- ¹⁹A. D. McLachlan and M. A. Ball, Rev. Mod. Phys. **36**, 844 (1964).
- ²⁰M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
- ²¹M. Hellgren and U. von Barth, Phys. Rev. B **78**, 115107 (2008).
- ²²A. Heßelmann and A. Görling, Molecular Physics **108**, 359 (2010).
- ²³J. F. Dobson, J. Wang, and T. Gould, Phys. Rev. B **66**, 081108 (2002); T. Gould and J. F. Dobson, Phys. Rev. A **85**, 062504 (2012).
- ²⁴T. Olsen and K. S. Thygesen, Phys. Rev. B **86**, 081103 (2012).
- ²⁵J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).
- ²⁶The choice of function is quite arbitrary and offers much scope for refinement.
- ²⁷T. Gould and J. F. Dobson, ArXiv e-prints (2012), arXiv:1206.6158 [physics.atom-ph].
- ²⁸S. J. Chakravorty, S. R. Gwaltney, E. R. Davidson, F. A. Parpia, and C. F. Fischer, Phys. Rev. A **47**, 3649 (1993).
- ²⁹J. M. Standard and P. R. Certain, J. Chem. Phys. **83**, 3002 (1985).