Correlation energies beyond the random-phase approximation: ISTLS applied to spherical atoms and ions

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The inhomogeneous Singwi, Tosi, Land and Sjolander (ISTLS) correlation energy functional of Dobson, Wang and Gould [PRB 66 081108(R) (2002)] has proved to be excellent at predicting correlation energies in semi-homogeneous systems, showing promise as a robust ‘next step’ fifth-rung functional by using dynamic correlation to go beyond the limitations of the direct random-phase approximation (dRPA), but with similar numerical scaling with system size. In this work we test the functional on spherically symmetric, neutral and charged atomic systems and find it gives excellent results (within 2mHa/e\(^{-}\) except Be) for the absolute correlation energies of the neutral atoms tested, and good results for the ions (within 4mHa/e\(^{-}\) except B\(^{+}\)). In all cases it performs better than the dRPA. When combined with the previous successes, these new results point to the ISTLS functional being a prime contender for high-accuracy, benchmark DFT correlation energy calculations.

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Since their development, density-functional theory[1, 2] (DFT) methods have vastly increased the range of quantum mechanical problems that can be studied. This wide range comes through the use of approximation to the exchange-correlation (xc) physics necessarily introduced to make Kohn-Sham (KS) theory possible. The most common approximations such as the LDA[2], GGA[3] and hybrid schemes[4] perform generally well, but usually give very poor results for electron correlation alone. In particular they give completely incorrect physics for van der Waals (vdW) dispersion physics, which governs the weak bonds between widely separated systems. This physics can be important in systems where there is a realm of near-zero density between sub-systems, such as in stretched molecules or lattices. The vdW physics is reintroduced in the popular vdW-DF[5] group of functionals, however such methods fail to reproduce the correct exponent[6] for vdW power laws of one term: the correlation energy, defined here through

\[
\delta E = E_{\text{KS}}(\delta n) - E_{\text{KS}}(0) - \frac{1}{2} \int d\mathbf{r} \frac{\partial^2}{\partial n^2} n_{2\text{Hc}}(\mathbf{r}, \mathbf{r}').
\]

The concept of the xc kernel can also be extended to current-response theory where the tensor kernel \(F^{xc}\) is known[11] to be a more ‘amenable’ functional of the density. In practice \(F^{xc}\) must be approximated, and the commonly employed dRPA involves setting \(f^{xc} \approx 0\). Perhaps surprisingly, the ACFD-dRPA functional has generally performed well for calculating energy differences, but not so well for absolute energies. Through the years various approximations have been proposed for the \(f^{xc}\) kernel, including the ALDA[12], energy-optimised kernel[13] and the Petersilka, Gossman and Gross exchange kernel[14]. These have met with varying degrees of success in different systems, but none has worked well in a wide range of systems. More recently the exact exchange kernel \(f^{xc} \approx f^x\) has been evaluated[15–18] in the time-dependent EXX (tdEXX) approach leading, via the ACFD functional, to excellent results for correlation energies of atoms and molecules.
\[O(N^5)/O(N^6)\) in molecular basis function language to calculate in practice, requiring inversion of the response or solutions of non-linear eigen-equations. Similarly, alternative approaches such as RPAX\[19\] and SOSEX\[20\] exist to improve on the ACFD-dRPA by including many-electron exchange but again these are numerically more difficult problems than the dRPA.

The ISTLS formalism\[21, 22,\] extending a total energy method for jellium\[23\] to general systems, was developed as a means of approximating the dynamic interactions in a sophisticated manner by making use of a self-consistent pair-correlation function. As shown in Ref. 22 it is equivalent to self-consistently approximating \(F^{xc}\) in an ACFD functional and it has so far enjoyed success in semi-homogeneous test systems\[21, 24-26\], most notably correctly reproducing the difficult transition from a three- to a two-dimensional metal, something the dRPA fails to do. In some sense the ISTLS represents the ‘next step’ of ACFD-like approximation: introducing self-consistent physics to the dynamic tdDFT calculation in a rigorous manner through \(F^{xc}\), rather than deriving \(f^{xc}\) or \(F^{xc}\) from the groundstate calculation.

In the original paper\[21\] on the method, the ISTLS functional was also tested on the helium atom where it performed very well, calculating the correlation energy to within 0.1mHa. Advances in computing power and improvements in numerical techniques have since allowed for wider testing. Here we discuss the implementation of the functional in spherical systems, and test it in a set of spherically symmetric neutral atoms and ions, including spin-polarised systems such as atomic sodium and lithium.

The Kohn-Sham equations \(\hat{h}\psi_i = \epsilon_i\psi_i\) can be used to generate the one-electron like orbitals of a system with a time-invariant KS potential \(V^{KS}\). In the absence of a magnetic field but the presence of a small perturbation to \(V^{KS}\) of form \(\delta V(r, t) = \delta V(r) e^{i\omega t}\) we can write the change in density of the system as \(\delta n = \int dr' \delta \chi_0(r, r'; \omega) \delta V(r') \equiv \int dr' \delta \nu_0(r, r'; \omega) \cdot \nabla \delta V(r')\) where \(\chi_0\) is the bare (non-interacting) density-density response of the system, and \(\nu_0\) is the bare vector response. The change in current can be defined via \(\delta j = i\omega \int dr' \nu_0(r, r'; \omega) \nabla \delta V(r')\) where \(\nu_0\) is the bare current-current response. Using tensor notation\[27\], it follows from these expressions that \(\chi_0 = -\nabla \cdot \nu_0\) and \(\nu_0 = -\nabla \cdot \psi\). Each of these has an interacting equivalent \(\chi\) which corresponds to the response a related system with electron-electron Coulomb interactions of strength \(\lambda\) but with the groundstate density unchanged. When \(\lambda = 1\) these are equivalent to the response of the system to a change in the external potential.

The ACFD correlation functional can be defined as

\[
E^c = \int_0^1 d\lambda \int_0^\infty \frac{d\nu}{\pi} \int dr dr' \Phi_\lambda(r, r', is) \tag{1}
\]

with integrand\[27\] \(\Phi_\lambda(r, r', \omega) = [\chi_\lambda - \chi_0(r, r'; \omega) e^{i(|r'| - r)}] = [\nu_\lambda - \nu_0(r, r'; \omega) \cdot \nabla \psi(|r'| - r)] = [\delta P_\lambda - \delta P_0(r, r'; \omega) : \nabla(|r'| - r)]\). Here \(e(R) = 1/R\) is the Coulomb potential and \(V(R) = -\nabla \otimes \nabla v(R)\) is its tensor equivalent. We can explicitly write the bare density-difference and density-current responses as

\[
\chi_0(r, r'; is) = 2R \sum_i f_i \psi_i^*(r) \psi_i(r') G_i(r, r') \tag{2}
\]

\[
\nu_0(r, r'; is) = \sum_i f_i [\psi_i^*(r) \psi_i(r') \nabla G_i(r, r') - G_i(r, r') \nabla \psi_i^*(r') \psi_i(r)]/\pi \tag{3}
\]

where \(G_i\) is short-hand for the bare one-electron Greens function \(G(r, r'; \epsilon_i + is)\), a solution of \([\hat{h} - \Omega]G(r, r'; \Omega) = \delta(r - r')\). The current-current response \(P_0\) has a similar expression. The interacting responses are defined via

\[
\chi_\lambda = \chi_0 + \chi_0 \ast (\lambda V + f^{xc}) \ast \chi_\lambda \tag{4}
\]

\[
P_\lambda = P_0 + P_0 \ast (\lambda V + F^{xc}) \ast P_\lambda \tag{5}
\]

where \(A \ast B \equiv \int d\epsilon A(r, \epsilon) B(\epsilon, r')\) and we take tensor products where appropriate. It is only in this relationship between the interacting and non-interacting case that the xc kernel is involved.

The ISTLS scheme can be written\[22\] as a tensor \(F^{xc}\) of form

\[
\lambda V + F^{xc}_\lambda = \frac{1}{2\pi} g_\lambda(r, r') \nabla \frac{\lambda}{|r - r'|} \otimes \nabla', \tag{6}
\]

\[
g_\lambda(r, r') = n_{2\lambda}(r, r')/|n(r)n(r')| \tag{7}
\]

where \(n_{2\lambda}\) is the interacting groundstate pair density at coupling strength \(\lambda\) and \(n\) is the groundstate density. Here we self-consistently calculate the dynamic interactions via the pair density \(n_{2\lambda}\) calculated by the fluctuation-dissipation theorem

\[
n_{2\lambda}(r', r') = n(r)n(r') - \delta(r - r') n^0(r) - \int \frac{d\lambda}{\pi} \chi_\lambda(r, r'; is), \tag{8}
\]

\[
\chi_\lambda(r, r'; is) = (\nabla \otimes \nabla') : P_\lambda(r, r'). \tag{9}
\]

In practice we must iterate these equations: i) set \(g_\lambda \approx g_0\) (ie. Hartree and exchange only) such that \(g_0(r, r') = 1 - [n^0(r)n^0(r')]^{-1} \sum_i f_i \psi_i^*(r) \psi_i^*(r')(r')^2\), ii) calculate \(P_\lambda\) via (5) and (6), iii) use \(P_\lambda\) to calculate a new \(g_\lambda\) via (8) and iv) use the new \(g_\lambda\) in ii) and repeat until convergence is reached.

Making use of (6) and (9) we can transform (5) into \(\chi_\lambda = \chi_0 + Q_\lambda \ast \chi_\lambda\) where \(Q_\lambda(r, r') = \int d\epsilon \nu_0(r, \epsilon) \cdot F^\lambda_\epsilon(r, \epsilon)\) and

\[
F^\lambda_\epsilon(r, \epsilon) = g_\lambda(r, r') \nabla \frac{\lambda}{|r - r'|}. \tag{10}
\]

Thus it is possible to evaluate the ISTLS equations using only \(\chi_0\) and \(P_0\) and not the full tensor current-current response \(P_0\). This form of the equations is the original\[21\] approach to ISTLS calculations. It should be noted that the Petersilka-Gossman-Gross (PGG) kernel\[14\]
can be defined in a similar manner with \( Q_{\lambda}(r, r') = \int \text{d}x \nu_0(r, x) \cdot \nabla_x g_0(x, r') \),
\[
\frac{\lambda}{|r - r'|} = \int \text{d}r \chi_0(r, x) \frac{\lambda_0(x, r')}{|r - r'|}.
\]

In spherically symmetric atoms we can separate the orbitals as \( \psi_i(r) \equiv \psi_{ilm}(r) = R_{nl}(r)Y_{lm}(\hat{r}) \) and \( \epsilon_i \equiv \epsilon_{nl} \) where \( Y_{lm} \) is a spherical harmonic function. The potential is \( V^K(r) \equiv V^K(r) \) and the radial function satisfies \( \hat{h}_l R_{nl}(r) = \epsilon_{nl} R_{nl}(r) \) where \( \hat{h}_l \equiv -\frac{1}{2} r^{-2} \partial_r r + l(l + 1) r^{-2} + V^K(r) \) and \( \partial_r \equiv \partial/\partial r \). It follows from the properties of spherical harmonics and the definition of the Greens function that \( \sum_{lm} \psi_{ilm}(r) \psi_{ilm}(r') = \frac{2\epsilon_{nl} + 1}{4\pi} P_l(x) \gamma_{nl}(r, r') \) and \( G(r, r'; \Omega) = \sum_{l} \frac{2\epsilon_{nl} + 1}{4\pi} P_l(x) G^0_l(r, r') \), where \( x = \hat{r} \cdot \hat{r} \), \( P_l(x) \) is a Legendre polynomial of order \( l \) and we use the short-hand notation \( \gamma_{nl}(r, r') = R_{nl}(r) R_{nl}(r') \). Here \( G^0_l \) satisfies \( [\hat{h} - \Omega] G^0_l(r, r') = \delta(r - r')/(rr') \). It also follows from the symmetry of the system that
\[
\chi_{\lambda}(r, r'; is) = \sum L \frac{2L+1}{4\pi} P_L(x) \chi_{\lambda L}(r, r' ; is )
\]
\[

\nu_{\lambda}(r, r'; is) = \sum L \frac{2L+1}{4\pi} P_L(x) [\nu'_{\lambda L} r' + \nu''_{\lambda L} r'] \]
\[
\text{where } r' = \hat{r} - (\hat{r} \cdot r) r = \hat{r} - x r'. \text{ Thus the response equation is diagonal in } l \text{ and } \chi_{\lambda L} = \chi_{\lambda L} + Q_{\lambda L} \chi_{\lambda L} \text{ where } A \ast B \equiv \int_0^\infty R^2 r^2 dr A(r, R) B(R, r').
\]

Making use of the orthogonality of the polynomials \( P_l(x) \) we define the bare (\( \lambda = 0 \)) responses through
\[
\chi_{0L}(r, r'; is) = \sum_{nl'} K_{ll'} [\beta_{nl'}] \chi_{0L}^r + i s \]
\[
\nu_{0L}(r, r'; is) = \sum_{nl'} K_{ll'} [\gamma_{nl'}] [\partial_r \chi_{0L}^r + i s] \]
\[
\nu_{0L}(r, r'; is) = \frac{1}{4\pi} \sum_{nl'} (\beta_{nl'} - \beta_{nl}) [\hat{r} \chi_{0L}^r + i s]
\]

The Clebsch-Gordan-like coefficients \( K_{ll'} \) and \( \beta_{ll'} \) are defined as \( K_{ll'} = \frac{2l + 1}{(2l + 1) (2l' + 1)} \int_0^1 \text{d}x P_l(x) P_{l'}(x) \) and \( \beta_{ll'} = \frac{2l + 1}{4\pi (2l + 1)} \int_0^1 \text{d}x D_l(x) P_l(x) \), where \( D_l = [\hat{r} P_l(x) \] where we can similarly expand the vector kernel (10) of the ISTLS scheme as \( F(r, r') = \sum L \frac{2L+1}{4\pi} P_L(x) [F_L^r(r, r') \hat{r} + F_L^l r'] \)
where \( F_L^r = \sum_{ll'} K_{ll'} g_{ll'} [\partial_r \psi_l] \) and \( F_L^l = \sum_{ll'} \beta_{ll'} g_{ll'} [\partial_l \psi_l] \). We define \( g_{ll'} \) through (7) and (8) but with \( \chi_{\lambda L}(r, r') \) only, and use the Legendre expansion of the Coulomb potential \( 1/|r - r'| = \sum_{l} \psi_l(r, r') (2l + 1) P_l(x) / 4\pi \) to define \( \psi_l = \frac{2l+1}{4\pi} \text{min}(r, r') \) max \( r, r' \) \(-l-1 \). Finally, using (12) and (16) we find[28] \( Q_{\lambda L} = [\nu_{0L} \ast r] F_L^r + \hat{r} [\nu_{0L} \ast r] F_L^l - [\hat{r} \nu_{0L} \ast r] F_L^l \]
where \( \hat{r} F_L = K_{L+1}^{-1} f_{L+1} + K_{L}^{-1} f_{L} \) for

We note that, with the exception of the self-consistency condition (defined via (8)), all terms are diagonal in \( s \) but couple together different \( l \) and involve convolutions over radial co-ordinate \( r \). This allows us to evaluate \( \chi_{\lambda L}(r, r'; is) \) from the sets \( \{ \chi_{0L}(r, r'; is) \} \) and \( \{ \nu_0(r, r'; is) \} \), provided the set \( g_{ll'} \) is already known. Once \( Q_{\lambda L}(r, r'; is) \) is calculated the system is diagonal in \( L \) and convolutions are only ever taken across \( r \). In spin-polarised systems we must also introduce spin \( \sigma = \uparrow, \downarrow \) such that all radial coordinates are replaced by \( rs \) and convolutions include a sum over spin.

To solve such a system numerically, we choose a grid of up to 512 radial points, and solve for the groundstate using the method of Krieger, Li and Iafrate[29] (KLI). The KLI approximation predicts \( E^{\text{KLI}} \) quite accurately, and reproduces the correct \(-1/r \) tail in atoms, a feature not present in LDA or GGA calculations. As such we feel it is an ideal starting point for these calculations.

The grid \( \{ r_i \} \), its weights \( \{ w_i \} \), the radial orbital wavefunctions \( R_{nl}(r) \), KS energies \( \epsilon_{nl} \), and the KS potential \( V^K(r) \) are then stored for later use in the calculation of \( \chi_0 \) and \( \nu_0 \). The Greens function can be solved quickly at arbitrary \( \lambda \) and \( \Omega \) via a shooting method such that
\[
G^0_l(r, r') = \frac{1}{2\pi r^2 Wr} \left\{ I(r) O(r') \right\} r < r'
\]
\[
O(r)I(r') \geq r'
\]
where \( Wr = I^0, O - O^0, I \) and \( O \) and \( I \) are “inner” or “outer” solutions of \( [\hat{h} - \Omega] X(r) = 0 \) with the boundary conditions \( I(r \to 0) \propto r^l \) and \( O(r \to \infty) = 0 \). Its radial derivative is then \( \partial_r G^0_l = D^0_l - G^0_l / r \) where
\[
D^0_l(r, r') = \frac{1}{2\pi r^2 Wr} \left\{ I(r) \partial_r O(r') \right\} r < r'
\]
\[
O(r)\partial_r I(r') \geq r'
\]

We choose a set of abscissae and weights for \( s \) based on a Clenshaw-Curtis quadrature scheme, chosen for its accuracy in integrating Lorentz functions, such that convergence is reached using at most 50 points. We also exploit the fact that the system is diagonal in \( s \) to calculate and store response functions at a single \( s \) only and cumulatively evaluate integrals for the pair density and correlation energy. The method is also diagonal in \( \lambda \) and we solve to high accuracy using \( \lambda = \frac{1}{2}, \frac{3}{2}, 1 \) with appropriate weights. We must also choose a cutoff in \( L \) which we set at \( L_{\text{max}} = 6 \). In all tested cases the contribution to the energy from the \( L = 5 \) term is under 0.5\%, with at least 97\% of the energy accounted for by \( L \leq 3 \).

Calculations are thus performed as follows: 1) for each \( l \) form the matrices \( \chi_{0L}(r_j, r_j; is) \), \( \nu_{0L}(r_j, r_j; is) \) and \( \nu_{0L}(r_j, r_j; is) \); and, at the first iteration, \( g_{ll'} \approx g_{ll'}(r_j, r_j); 2) take the stored response functions and pair densities \( \{ g_{ll'} \} \), then use quadrature to form \( Q_{\lambda L}(r_j, r_j) \) via (17); 3) solve the matrix equation \( \chi_{Lij} = \chi_{0Lij} + \sum_k Q_{Li,ik} \nu_k \chi_{L,ij} \), repeating 1-3) for each \( L \) and each \( s \) 4) calculate new values for \( \{ g_{ll'} \} \) through a weighted mix of the existing data and the newly evaluated \( \{ \nu_{0L} \} \) (via (8)) \( \{ g_{ll'} \}; 5) repeat from 1) until converged; 6) reset \( g_{ll'} \)
and repeat from 1) for a new $\lambda$. Typically it takes between four and six iterations mixing 70% new and 30% old pair density to converge a correlation energy. It is worth noting that at each stage we impose symmetry under exchange of $r$ and $r'$ on each $g_{\lambda l}$. While formally this may differ slightly from the true ISTLS method, tests indicate that the correlation energy remains virtually unchanged, while convergence is improved.

From Ref. 15, and with ‘exact’ correlation energies from benchmark methods[30–33]. We also include an extrapolation.

TABLE I. Correlation energies (in -mHa) for spherical atoms and ions. Includes the mean absolute error % (MAE%) for the neutral atoms (N), ions (I) and all atoms and ions together. He$^+$ is the extrapolation to $Z = \infty$ for a two-electron system.

| Atom | RPA | PGG | ISTLS | tdEXX$^a$ | Exact$^b$ |
|------|-----|-----|-------|----------|----------|
| He   | 84.0| 44.9| 42.3  | 44       | 42.0     |
| Li   | 113 | 49  | 41    | -        | 45       |
| Be   | 181 | 104 | 79    | 102      | 94       |
| N    | 336 | 145 | 191   | -        | 188      |
| Ne   | 585 | 331 | 405   | 389      | 390      |
| Na   | 612 | 329 | 413   | -        | 396      |
| Mg   | 672 | 374 | 458   | 445      | 438      |
| P    | 833 | 418 | 563   | -        | 540      |
| Ar   | 1071| 578 | 744   | 721      | 722      |
| MAE% N | 76 | 15 | 5 | - | - |
| H$^-$ | 74.9 | 43.6 | 36.4 | - 42.0 |
| Li$^+$ | 86.7 | 45.3 | 42.8 | - 43.1 |
| Be$^{2+}$ | 88.3 | 45.6 | 43.7 | - 44.3 |
| Ne$^{8+}$ | 91.1 | 46.1 | 45.4 | - 44.7 |
| Hg$^{78+}$ | 92.4 | 46.3 | 46.2 | - 46.5 |
| He$^+$ | 92.7 | 46.4 | 46.4 | - 46.9 |
| Be$^+$ | 124 | 51 | 37 | - | 47 |
| Li$^-$ | 146 | 84 | 69 | - | 73 |
| B$^+$ | 207 | 120 | 86 | - | 111 |
| Na$^+$ | 582 | 323 | 404 | - | 389 |
| Mg$^+$ | 623 | 331 | 422 | - | 400 |
| MAE% I | 94 | 7 | 7 | - | - |
| MAE% | 86 | 11 | 6 | - | - |

$^a$ From Ref. 15, $^b$ From Refs 30–33

In Table I we present correlation energies for a variety of spherically symmetric systems. We compare the ISTLS energies with those from the dRPA and PGG calculated using the same code, with tdEXX energies from Ref. 15, and with ‘exact’ correlation energies from benchmark methods[30–33]. We also include an extrapolation to the $Z = \infty$ case for the Helium isoelectronic series (labeled He$^+$) by fitting $E_c(Z)$ vs. $1/Z$ for $Z \geq 3$. We have included only those atoms and ions that converged under the ISTLS self-consistency loop with a reasonable mixing coefficient and thus reasonable time. For benchmarking we compared our dRPA results with those of Jiang and Engel[31] and found agreement well within expected methodological bounds.

In general the ISTLS does very well for correlation energies, outperforming the dRPA in all tested systems, and the PGG in all but a few systems. In all the systems bar He where comparable tdEXX results were available[15] it outperforms the ISTLS, however this accuracy comes at much greater computational expense. ISTLS performs less well for ions than for atoms, with the greatest error in Be$^+$ and B$^+$. It is possible that, in these cases, the ISTLS iterations converge to an incorrect result, however testing this is difficult. For C$^{2+}$ the ISTLS method did not converge at all, most likely due to numerical instabilities in the high-density core region. It is worth noting that the ISTLS always pulls the PGG results back towards the true value, albeit overly so in some cases. While the PGG approximation performs slightly better than ISTLS for some of the smaller systems tested here, it is known to break down in bulk systems, particularly low density metals where it under-correlates[34]. This failure can be seen in the trend presented here, where the relative absolute PGG error increases with system size while ISTLS improves. By contrast the ISTLS performs consistently well for jellium[23], metallic surface energies[24], across two- and three-dimensional metals[25], and here in the spherical atoms and ions.

The numerical cost of the ISTLS functional scales with system size in a similar manner to standard ACFD-dRPA methods, but with a larger pre-factor and slightly larger memory requirements. In the best case scenario, the ISTLS can scale as $O(N^4)$, while tdEXX and RPAx can scale as $O(N^5)$, a saving of one order. Our ISTLS calculations took between ten and twenty times as long as the ACFD-dRPA and used around five times the memory. The detailed method presented here may point the way to implementation in more general geometries involving expansions on Gaussian-type and Slater-type orbitals[35]. Implementation in existing plane-wave based bulk ACFD-dRPA codes should also be possible, albeit with non-trivial changes.

Overall, we believe that the ISTLS is an excellent candidate for a ‘next step’ functional, going beyond the dRPA. The tests on spherical systems further confirm its versatility, showing accurate results in systems with vastly different physics to those previously tested. With work on efficiencies and implementation it could, in future, provide viable benchmark calculations for electronic systems where existing high-level methods, such as the popular ACFD-dRPA, fail to achieve the desired level of accuracy and where wavefunction methods are too difficult.

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