

# Correlation energies beyond the random-phase approximation: Inhomogeneous Singwi-Tosi-Land-Sjolander functional 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 [Phys. Rev. B **66**, 081108(R) (2002)] has proved to be successful at predicting correlation energies in semihomogeneous 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  $2\text{mHa}/e^-$  except Be) for the absolute correlation energies of the neutral atoms tested, and good results for the ions (within  $4\text{mHa}/e^-$  except  $\text{B}^+$ ). In all cases it performs better than the dRPA. When combined with the previous successes, these new results point to the ISTLS functional being potentially suitable for high-accuracy, benchmark DFT correlation energy calculations in a wide range of systems.

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## I. INTRODUCTION

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 subsystems, 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  $U = -C_p D^{-p}$  in zero-gap systems with at least one long and one short dimension, such as thin slab geometries and nanowires [7].

An alternative approach to total energy calculations is to (i) solve for a ground state under a given scheme (e.g., LDA) to evaluate  $V^{\text{KS}}(\mathbf{r})$  and, via the KS Hamiltonian  $\hat{h} = -\frac{1}{2}\nabla^2 + V^{\text{KS}}(\mathbf{r})$ , to evaluate the orbitals and KS energies through  $\hat{h}\psi_i = \epsilon_i\psi_i$  and the density through  $n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$  where  $f_i$  is the occupation number of orbital  $i$ ; (ii) recalculate the energy using the so-called exact exchange (EXX) functional for exchange and a different functional for correlation. Here we use the Hartree and exchange pair density  $n_{2\text{Hx}}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') - |\sum_i f_i \psi_i(\mathbf{r})\psi_i(\mathbf{r}')|^2$  to define the energy terms  $E^{\text{H}} + E^{\text{x}} = \frac{1}{2} \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} n_{2\text{Hx}}(\mathbf{r}, \mathbf{r}')$  and we set the EXX total energy to  $E^{\text{EXX}} = \int d\mathbf{r} [-\frac{1}{2} \sum_i \psi_i(\mathbf{r})\nabla^2\psi_i(\mathbf{r}) + n(\mathbf{r})V^{\text{KS}}(\mathbf{r})] + E^{\text{H}} + E^{\text{x}}$ .

Thus the total energy of a given system can be calculated exactly from the KS potential, with the exception of one term: the correlation energy, defined here through  $E^{\text{c}} = E - E^{\text{EXX}}$  where  $E$  is the true ground-state energy of the system. The correlation energy term essentially bundles the “difficult”

physics of the true many-electron system into a single term, which is a highly nonlocal functional of the density and/or Kohn-Sham orbital wave functions, and must be approximated. An *ab initio* way to evaluate correlation energies is to use time-dependent DFT [8] via the linear density-response function, the fluctuation-dissipation theorem, and the adiabatic connection formula to form the “ACFD” functional. In recent years there has been a large increase in the use of ACFD functionals, particularly for the evaluation of vdW dispersion. The majority of these also make use of the direct random-phase approximation (dRPA) which we define later. A good discussion on, and summary of the ACFD-dRPA approach can be found in Ref. [9], although initial calculations on inhomogeneous systems were carried out more than a decade ago [10].

Theoretically exact applications of the ACFD involve the unknown dynamic exchange-correlation kernel  $f^{\text{xc}}$ , a two-point function defined as the second functional derivative of the xc energy via  $f^{\text{xc}}(\mathbf{r}, \mathbf{r}'; t - t') = \delta^2 E^{\text{xc}} / [\delta n(\mathbf{r}, t)\delta n(\mathbf{r}', t')]$ . The concept of the xc kernel can also be extended to current-response theory where the tensor kernel  $\mathbf{F}^{\text{xc}}$  is known [11] to be a more “amenable” functional of the density. In practice  $f^{\text{xc}}$  must be approximated, and the commonly employed dRPA involves setting  $f^{\text{xc}} \approx 0$ . 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  $f^{\text{xc}}$  kernel, including the ALDA [12], energy-optimized kernel [13], and the Petersilka, Gossmann, 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  $f^{\text{xc}} \approx f^{\text{x}}$  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. However this kernel is very difficult [ $O(N^5)/O(N^6)$  in molecular basis function language] to calculate in practice, requiring inversion of the response or solutions of nonlinear eigenequations. 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.

## II. THE ISTLS METHOD

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  $F^{\text{xc}}$  in an ACFD functional and it has so far enjoyed success in semihomogeneous 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  $F^{\text{xc}}$ , rather than deriving  $f^{\text{xc}}$  or  $F^{\text{xc}}$  from the ground-state 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 0.1 mHa. 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-polarized systems such as atomic sodium and lithium.

## III. ISTLS FORMALISM FOR MULTI-ELECTRON ATOMS

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  $V^{\text{KS}}$ . In the absence of a magnetic field but the presence of a small perturbation to  $V^{\text{KS}}$  of form  $\delta V(\mathbf{r}, t) = \delta V(\mathbf{r})e^{i\omega t}$  we can write the change in density of the system as  $\delta n = \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}'; \omega) \delta V(\mathbf{r}') \equiv \int d\mathbf{r}' \mathbf{v}_0(\mathbf{r}, \mathbf{r}'; \omega) \cdot \nabla \delta V(\mathbf{r}')$  where  $\chi_0$  is the bare (noninteracting) density-density response of the system, and  $\mathbf{v}_0$  is the bare vector response. The change in current can be defined via  $\delta \mathbf{j} = i\omega \int d\mathbf{r}' \mathbf{P}_0(\mathbf{r}, \mathbf{r}'; \omega) \nabla \delta V(\mathbf{r}')$  where  $\mathbf{P}_0$  is the bare current-current response. Using tensor notation,<sup>1</sup> it follows from these expressions that  $\chi_0 = -\nabla' \cdot \mathbf{v}_0$  and  $\mathbf{v}_0 = -\nabla \cdot \mathbf{P}$ . Each of these has an interacting equivalent (e.g.,  $\chi_\lambda$ ), which corresponds to the response a related system with electron-electron Coulomb interactions of strength  $\lambda$  but with the ground-state 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

$$E^c = \int_0^1 d\lambda \int_0^\infty \frac{ds}{\pi} \int d\mathbf{r} d\mathbf{r}' \Phi_\lambda(\mathbf{r}, \mathbf{r}', is), \quad (1)$$

<sup>1</sup>Here and henceforth we define indices  $\mu, \nu \in (x, y, z)$ , vectors to be bold  $\mathbf{v}$ , and tensors to be upright sans-serif T. The tensor  $\mathbf{T} = \mathbf{v} \otimes \mathbf{u}$  has elements  $T_{\mu\nu} = v_\mu u_\nu$ , the vector  $\mathbf{u} = \mathbf{v} \cdot \mathbf{T}$  has elements  $u_\mu = v_\nu T_{\nu\mu}$ , and  $\mathbf{A} : \mathbf{B} = \sum_{\mu\nu} A_{\mu\nu} B_{\nu\mu}$  is scalar.

with integrand<sup>1</sup>  $\Phi_\lambda(\mathbf{r}, \mathbf{r}', \omega) = [\chi_\lambda - \chi_0](\mathbf{r}, \mathbf{r}'; \omega) v(|\mathbf{r}' - \mathbf{r}|) \equiv [\mathbf{v}_\lambda - \mathbf{v}_0](\mathbf{r}, \mathbf{r}'; \omega) \cdot \nabla' v(|\mathbf{r}' - \mathbf{r}|) \equiv [\mathbf{P}_\lambda - \mathbf{P}_0](\mathbf{r}, \mathbf{r}'; \omega) : \mathbf{V}(|\mathbf{r}' - \mathbf{r}|)$ . Here  $v(R) = 1/R$  is the Coulomb potential and  $\mathbf{V}(R) = -\nabla \otimes \nabla v(R)$  is its tensor equivalent. We can explicitly write the bare density-density and density-current responses as

$$\chi_0(\mathbf{r}, \mathbf{r}'; is) = 2\text{Re} \sum_i f_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') G_i(\mathbf{r}, \mathbf{r}'), \quad (2)$$

$$\mathbf{v}_0(\mathbf{r}, \mathbf{r}'; is) = \text{Im} \sum_i f_i [\psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') \nabla' G_i(\mathbf{r}, \mathbf{r}') - G_i(\mathbf{r}, \mathbf{r}') \nabla' \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}')]/s, \quad (3)$$

where  $G_i$  is short-hand for the bare one-electron Greens function  $G(\mathbf{r}, \mathbf{r}'; \epsilon_i + is)$ , a solution of  $[\hat{h} - \Omega]G(\mathbf{r}, \mathbf{r}'; \Omega) = \delta(\mathbf{r} - \mathbf{r}')$ . The current-current response  $\mathbf{P}_0$  has a similar expression. The interacting responses are defined via

$$\chi_\lambda = \chi_0 + \chi_0 \star (\lambda v + f_\lambda^{\text{xc}}) \star \chi_\lambda, \quad (4)$$

$$\mathbf{P}_\lambda = \mathbf{P}_0 + \mathbf{P}_0 \star (\lambda \mathbf{V} + \mathbf{F}_\lambda^{\text{xc}}) \star \mathbf{P}_\lambda, \quad (5)$$

where  $A \star B \equiv \int d\mathbf{x} A(\mathbf{r}, \mathbf{x}) B(\mathbf{x}, \mathbf{r}')$  and we take tensor products where appropriate. It is only in this relationship between the interacting and noninteracting case that the xc kernel is involved.

The ISTLS scheme can be written [22] as a tensor  $F^{\text{xc}}$  of the form,

$$\lambda \mathbf{V} + \mathbf{F}_\lambda^{\text{xc}} = \frac{1}{s^2} g_\lambda(\mathbf{r}, \mathbf{r}') \nabla \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|} \otimes \nabla', \quad (6)$$

$$g_\lambda(\mathbf{r}, \mathbf{r}') = n_{2\lambda}(\mathbf{r}, \mathbf{r}')/[n(\mathbf{r})n(\mathbf{r}')], \quad (7)$$

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

$$n_{2\lambda}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r})n(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')n^0(\mathbf{r}) - \int \frac{ds}{\pi} \chi_\lambda(\mathbf{r}, \mathbf{r}'; is), \quad (8)$$

$$\chi_\lambda(\mathbf{r}, \mathbf{r}'; is) = (\nabla \otimes \nabla') : \mathbf{P}_\lambda(\mathbf{r}, \mathbf{r}'). \quad (9)$$

In practice we must iterate these equations: (i) set  $g_\lambda \approx g_0$  (i.e., Hartree and exchange only) such that  $g_0(\mathbf{r}, \mathbf{r}') = 1 - [n^0(\mathbf{r})n^0(\mathbf{r}')]^{-1} |\sum_i f_i \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}')|^2$ , (ii) calculate  $\mathbf{P}_\lambda$  via (5) and (6), (iii) use  $\mathbf{P}_\lambda$  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  $\chi_\lambda = \chi_0 + \mathcal{Q}_\lambda \star \chi_\lambda$  where  $\mathcal{Q}_\lambda(\mathbf{r}, \mathbf{r}') = \int d\mathbf{x} \mathbf{v}_0(\mathbf{r}, \mathbf{x}) \cdot \mathbf{F}_\lambda(\mathbf{x}, \mathbf{r}')$  and

$$\mathbf{F}_\lambda(\mathbf{r}, \mathbf{r}') = g_\lambda(\mathbf{r}, \mathbf{r}') \nabla \frac{\lambda}{|\mathbf{r} - \mathbf{r}'|}. \quad (10)$$

Thus it is possible to evaluate the ISTLS equations using only  $\chi_0$  and  $\mathbf{v}_0$  and not the full tensor current-current response  $\mathbf{P}_0$ . This form of the equations is the original [21] approach to ISTLS calculations. It should be noted that the Petersilka-Gossmann-Gross (PGG) kernel [14] can be defined in a similar manner with  $\mathcal{Q}_\lambda(\mathbf{r}, \mathbf{r}') = \int d\mathbf{x} \mathbf{v}_0(\mathbf{r}, \mathbf{x}) \cdot \nabla_x [g_0(\mathbf{x}, \mathbf{r}') \frac{\lambda}{|\mathbf{x} - \mathbf{r}'|}] \equiv \int d\mathbf{r} \chi_0(\mathbf{r}, \mathbf{x}) \frac{\lambda g_0(\mathbf{x}, \mathbf{r}')}{|\mathbf{x} - \mathbf{r}'|}$ .

In spherically symmetric atoms we can separate the orbitals as  $\psi_i(\mathbf{r}) \equiv \psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$  and  $\epsilon_i \equiv \epsilon_{nl}$  where

$Y_{lm}$  is a spherical harmonic function. The potential is  $V^{\text{KS}}(\mathbf{r}) \equiv V^{\text{KS}}(r)$  and the radial function satisfies  $\hat{h}_l R_{nl}(r) = \epsilon_{nl} R_{nl}(r)$  where  $\hat{h}_l \equiv -\frac{1}{2}\{r^{-1}\partial_r \partial_r r - l(l+1)r^{-2}\} + V^{\text{KS}}(r)$  and  $\partial_r \equiv \partial/\partial r$ . It follows from the properties of spherical harmonics and the definition of the Greens function that  $\sum_m \psi_{nlm}^*(\mathbf{r})\psi_{nlm}(\mathbf{r}') = \frac{2l+1}{4\pi} P_l(x)\gamma_{nl}(r,r')$  and  $G(\mathbf{r},\mathbf{r}';\Omega) = \sum_l \frac{2l+1}{4\pi} P_l(x)G_l^\Omega(r,r')$  where  $x = \hat{\mathbf{r}} \cdot \hat{\mathbf{r}}'$ ,  $P_l(x)$  is a Legendre polynomial of order  $l$  and we use the short-hand  $\gamma_{nl}(r,r') = R_{nl}(r)R_{nl}(r')$ . Here  $G_l^\Omega$  satisfies  $[\hat{h}_l - \Omega]G_l^\Omega(r,r') = \delta(r-r')/(rr')$ . It also follows from the symmetry of the system that

$$\chi_\lambda(\mathbf{r},\mathbf{r}';is) = \sum_L \frac{2L+1}{4\pi} P_L(x)\chi_{\lambda L}(\mathbf{r},\mathbf{r}';is), \quad (11)$$

$$\mathbf{v}_\lambda(\mathbf{r},\mathbf{r}';is) = \sum_L \frac{2L+1}{4\pi} P_L(x)[v_{\lambda L}^r \hat{\mathbf{r}} + v_{\lambda L}^\perp \mathbf{r}'_\perp], \quad (12)$$

where  $\mathbf{r}'_\perp = \hat{\mathbf{r}} - (\hat{\mathbf{r}} \cdot \hat{\mathbf{r}}')\hat{\mathbf{r}}' = \hat{\mathbf{r}} - x\hat{\mathbf{r}}'$ . Thus the response equation is diagonal in  $L$  and  $\chi_{\lambda L} = \chi_{0L} + Q_{\lambda L} \star \chi_{\lambda L}$  where  $A \star B \equiv \int_0^\infty R^2 dR A(R,R)B(R,r')$ .

Making use of the completeness of the polynomials  $P_l(x)$  we define the bare ( $\lambda = 0$ ) responses through

$$\chi_{0L}(\mathbf{r},\mathbf{r}';is) = 2 \sum_{nl'} K_{ll'}^L \gamma_{nl} \text{Re} G_{l'}^{\epsilon_{nl}+is}, \quad (13)$$

$$v_{0L}^r(\mathbf{r},\mathbf{r}';is) = \frac{1}{s} \sum_{nl'} K_{ll'}^L \{ \gamma_{nl} [\partial_{r'} \text{Im} G_{l'}^{\epsilon_{nl}+is}] - [\partial_{r'} \gamma_{nl}] \text{Im} G_{l'}^{\epsilon_{nl}+is} \}, \quad (14)$$

$$v_{0L}^\perp(\mathbf{r},\mathbf{r}';is) = \frac{1}{sr'} \sum_{nl'} (\beta_{l'l}^L - \beta_{ll'}^L) \gamma_{nl} \text{Im} G_{l'}^{\epsilon_{nl}+is}. \quad (15)$$

The Clebsch-Gordan-like coefficients  $K_{ll'}^L$  and  $\beta_{ll'}^L$  are defined as  $K_{ll'}^L = \frac{(2l+1)(2l'+1)}{4\pi(2L+1)} \int_{-1}^1 dx P_l P_{l'} P_L$  and  $\beta_{ll'}^L = \frac{(2l+1)(2l'+1)}{4\pi(2L+1)} \int_{-1}^1 dx D_l P_{l'} P_L$  where  $D_l \equiv [\partial_x P_l(x)]$ . We can similarly expand the vector kernel (10) of the ISTLS scheme as

$$\mathbf{F}(\mathbf{r},\mathbf{r}') = \sum_L \frac{2L+1}{4\pi} P_L(x) [F_L^r(\mathbf{r},\mathbf{r}')\hat{\mathbf{r}} + F_L^\perp \mathbf{r}'_\perp], \quad (16)$$

where  $F_L^r = \sum_{ll'} K_{ll'}^L g_{\lambda l} [\partial_r v_{l'}]$  and  $F_L^\perp = \sum_{ll'} \beta_{l'l}^L g_{\lambda l} v_{l'}/r$ . We define  $g_{\lambda l}$  through (7) and (8) but with  $\chi_{\lambda l}(\mathbf{r},\mathbf{r}')$  only, and use the Legendre expansion of the Coulomb potential  $1/|\mathbf{r}-\mathbf{r}'| = \sum_l v_l(r,r') \frac{(2l+1)P_l(x)}{4\pi}$  to define  $v_l = \frac{4\pi}{2l+1} \min(r,r')^l \max(r,r')^{-(l+1)}$ . Finally, using (12) and (16) we find [27]

$$Q_{\lambda L} = v_{0L}^r \star F_L^r + \hat{\kappa} [v_{0L}^\perp \star F_L^\perp] - [\hat{\kappa} v_{0L}^\perp] \star [\hat{\kappa} F_L^\perp], \quad (17)$$

where  $\hat{\kappa} f_L \equiv K_{L+1}^{L+1} f_{L+1} + K_{L-1}^{L-1} f_{L-1}$ .

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 coordinate  $r$ . This allows us to evaluate  $\chi_{\lambda L}(\mathbf{r},\mathbf{r}';is)$  from the sets  $\{\chi_{0l}(\mathbf{r},\mathbf{r}';is)\}_l$  and  $\{v_{0l}(\mathbf{r},\mathbf{r}';is)\}_l$  provided the set  $\{g_{\lambda l}\}_l$  is already known. Once  $Q_{\lambda L}(\mathbf{r},\mathbf{r}';is)$  is calculated the system is diagonal in  $L$  and convolutions are only ever taken across  $r$ . In spin-polarized systems we must also introduce spin  $\sigma = \uparrow\downarrow$  such that all radial coordinates are replaced by  $r\sigma$  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 ground state using the method of Krieger, Li, and Iafate [28] (KLI). The KLI approximation predicts  $E^{\text{EXX}}$  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 wave functions  $R_{nl}(r_i)$ , KS energies  $\epsilon_{nl}$ , and the KS potential  $V^{\text{KS}}(r_i)$  are then stored for later use in the calculation of  $\chi_0$  and  $\mathbf{v}_0$ . The Greens function can be solved quickly at arbitrary  $l$  and  $\Omega$  via a shooting method such that

$$G_l^\Omega(r,r') = \frac{1}{2rr'Wr} \begin{cases} I(r)O(r') & r < r' \\ O(r)I(r') & r \geq r' \end{cases}, \quad (18)$$

where  $Wr = I\partial_r O - O\partial_r I$  and  $I(r)$  and  $O(r)$  are ‘‘inner’’ or ‘‘outer’’ solutions of  $[\hat{h}_l - \Omega]X(r) = 0$  with the boundary conditions  $I(r \rightarrow 0) \propto r^l$  and  $O(r \rightarrow \infty) = 0$ . Its radial derivative is then  $\partial_{r'} G_l^\Omega = D_l^\Omega - G_l^\Omega/r'$  where

$$D_l^\Omega(r,r') = \frac{1}{2rr'Wr} \begin{cases} I(r)\partial_r O(r') & r < r' \\ O(r)\partial_r I(r') & r \geq r' \end{cases}. \quad (19)$$

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  $\lambda = \frac{1}{3}, \frac{2}{3}, 1$  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  $\chi_{0l}(r_i, r_j; is)$ ,  $v_{0l}^r(r_i, r_j; is)$ , and  $v_{0l}^\perp(r_i, r_j; is)$  and, at the first iteration,  $g_{\lambda l} \approx g_{0l}(r_i, r_j)$ ; (2) take the stored response functions and pair densities  $\{g_{\lambda l}\}_l$ , then use quadrature to form  $Q_{\lambda L}(r_i, r_j)$  via (17); (3) solve the matrix equation  $\chi_{\lambda Lij} = \chi_{0Lij} + \sum_k Q_{\lambda Lik} w_k \chi_{\lambda Lkj}$ , repeating (1)–(3) for each  $L$  and each  $s$  (4) calculate new values for  $\{g_{\lambda l}\}_l$  through a weighted mix of the existing data and the newly evaluated [via (8)]  $\{g_{\lambda l}\}_l$ ; (5) repeat from (1) until converged; (6) reset  $\{g_{\lambda l}\}$  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.

#### IV. NUMERICAL RESULTS

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 [29–32]. We also include an extrapolation to the  $Z = \infty$  case

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 <sup>a</sup>	Exact <sup>b</sup>
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 <sup>-</sup>	74.9	43.6	36.4	—	42.0
Li <sup>+</sup>	86.7	45.3	42.8	—	43.1
Be <sup>2+</sup>	88.3	45.6	43.7	—	44.3
Ne <sup>8+</sup>	91.1	46.1	45.4	—	44.7
Hg <sup>78+</sup>	92.4	46.3	46.2	—	46.5
He*	92.7	46.4	46.4	—	46.9
Be <sup>+</sup>	124	51	37	—	47
Li <sup>-</sup>	146	84	69	—	73
B <sup>+</sup>	207	120	86	—	111
Na <sup>+</sup>	582	323	404	—	389
Mg <sup>+</sup>	623	331	422	—	400
MAE% I	94	7	7	—	
MAE%	86	11	6	—	

<sup>a</sup>From Ref. [15];

<sup>b</sup>From Refs. [29–32].

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 [30] 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<sup>+</sup> and B<sup>+</sup>. It is possible that, in these cases, the ISTLS iterations converge to an incorrect result, however, testing this is difficult. For C<sup>2+</sup> 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 undercorrelates [33]. 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 prefactor 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 10 and 20 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 [34]. Implementation in existing plane-wave-based bulk ACFD-dRPA codes should also be possible, albeit with nontrivial changes.

## V. CONCLUSIONS

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 the 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 wave-function methods are too difficult.

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