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Self-interaction in Green's-function theory of the hydrogen atom

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Atomic hydrogen provides a unique test case for computational electronic structure methods, since its electronic excitation energies are known analytically. With only one electron, hydrogen contains no electronic correlation and is therefore particularly susceptible to spurious self-interaction errors introduced by certain computational methods. In this paper we focus on many-body perturbation-theory (MBPT) in Hedin's *GW* approximation. While the Hartree-Fock and the exact MBPT self-energy are free of self-interaction, the correlation part of the *GW* self-energy does not have this property. Here we use atomic hydrogen as a benchmark system for *GW* and show that the self-interaction part of the *GW* self-energy, while non-zero, is small. The effect of calculating the *GW* self-energy from exact wavefunctions and eigenvalues, as distinct from those from the local-density approximation, is also illuminating.

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I. INTRODUCTION

Ab initio many-body quantum mechanical calculations are crucially important to our understanding of the behavior of atomic, molecular and condensed matter systems. It is well known that prediction of the behavior of these systems requires the description of electronic correlation. Whilst density-functional theory (DFT) in the local-density approximation (LDA) does this with startling success in many cases, it does so at the expense of a non-physical electron self-interaction. For delocalized electron systems this self-interaction becomes negligible, but in atomic or strongly localized electronic systems it plays an important role. If one is interested in the calculation of quasiparticle excitation spectra, many-body perturbation-theory (MBPT) is formally a correct way to proceed. For solids, MBPT in Hedin's *GW* approximation [1] has become the method of choice, but it is also increasingly being applied to molecular systems and clusters. The *GW* self-energy can be decomposed into correlation and exchange parts, where the latter is the same as the Fock operator encountered in Hartree-Fock theory and thus self-interaction free. While the exact self-energy must also be free of self-interaction, the correlation part of the *GW* self-energy does not have this property. To investigate the influence of self-interaction in the *GW* approach the hydrogen atom provides an ideal case, because the exact solution is known analytically.

Hydrogen in its solid phase has previously been studied within the *GW* approximation by Li *et al.* [2], who analyzed the transition between the high-pressure solid phase and the low density, atomic-like limit. For individual atoms, *GW* electron removal and addition energies (we use the term "quasiparticle" energies by analogy with the solid-state situation) have been investigated by Shirley and Martin [3], Dahlen *et al.* [4, 5], Stan *et al.* [6] and Delaney *et al.* [7], although hydrogen was not considered. These studies have shown that *GW*, in general, gives quasiparticle properties which are much improved over DFT and Hartree-Fock methods, even for atoms.

In this paper we use the hydrogen atom as a benchmark system to quantify the self-interaction error in the *GW* approach. Since the self-energy diagrams *beyond GW*, known as the vertex correction, must by definition correct this self-interaction error, our findings are relevant for research into vertex functions for the many-electron problem.

Attention has recently focused on the prospects for improving the usual non-self-consistent *GW* calculations by choosing an initial Green's function, G_0, that is physically more reasonable than the LDA (e.g. [2, 8, 9]). We explore this here by determining the sensitivity of the self-interaction error to the use of the exact hydrogenic orbitals and energies in place of those from the local-density approximation (LDA). We also assess the error introduced into *GW* calculations by employing first-order perturbation theory in solving the quasiparticle equation (as opposed to the full numerical solution), and we analyze the quasiparticle wavefunctions that emerge from a full solution.

II. HARTREE-FOCK VS. DFT-LDA

In many-body perturbation theory the quasiparticle excitation energies $\epsilon_{i\sigma}$ and wavefunctions $\psi_{i\sigma}$ are the so-

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lutions of the quasiparticle equation

$$H_0(\mathbf{r})\psi_{i\sigma}(\mathbf{r})+\sum_{\sigma'}\int d\mathbf{r}' M_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\epsilon_{i\sigma}^{\mathrm{qp}})\psi_{i\sigma'}(\mathbf{r}') = \epsilon_{i\sigma}^{\mathrm{qp}}\psi_{i\sigma}(\mathbf{r}) \tag{1}$$

where, in Hartree atomic units, $H_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r})$ and $v_{ext}(\mathbf{r})$ is the external potential. It is customary to divide the mass operator M into the local Hartree potential (v_H) and the non-local self-energy (Σ)

$$M_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\epsilon) = v_H(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\delta_{\sigma\sigma'} + \Sigma_{\sigma\sigma'}(\mathbf{r},\mathbf{r}';\epsilon). \tag{2}$$

Omitting correlation contributions from Σ yields the exact-exchange or Hartree-Fock case, where the self-energy takes the form

$$\Sigma^x_{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = -\sum_i^{occ} \frac{\psi_{i\sigma}(\mathbf{r})\psi^*_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\delta_{\sigma\sigma'} \tag{3}$$

and the Hartree potential is given by

$$v_H(\mathbf{r}) = \sum_{i,\sigma}^{occ}\int d\mathbf{r}' \frac{\psi_{i\sigma}(\mathbf{r}')\psi^*_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{4}$$

Since the sum runs over all occupied states the Hartree potential contains an artificial interaction of electrons with themselves. For the hydrogen atom this so-called self-interaction of the electron is the *only* content of the Hartree potential and may be calculated analytically using the exact ground-state wavefunction

$$\psi^{\uparrow}_{1s}(r) = \frac{1}{\sqrt{\pi}}e^{-r} \tag{5}$$

as

$$v_H(r) = \frac{1}{r}\left\{1-(1+r)\,e^{-2r}\right\}. \tag{6}$$

The self-interaction is a positive, decreasing function and hence tends to delocalize the wavefunction (i.e. incorrectly pushes its weight away from the nucleus).

In Hartree-Fock the self-interaction terms introduced in the Hartree potential are exactly canceled by the Fock operator Σ_x. This makes Hartree-Fock exact for one-electron systems such as the hydrogen atom. However, the lack of correlation renders Hartree-Fock unsuitable for many polyatomic systems of interest.

Of more practical use is Kohn-Sham [10] density-functional theory, which by virtue of the Hohenberg-Kohn theorem [11] establishes an exact and universal functional relationship between the ground-state density $n(\mathbf{r})$ and the total energy E of a system. Mapping the system of interacting electrons onto a fictitious system of non-interacting electrons, that reproduces the exact density, yields the Kohn-Sham equations:

$$\left[H_0(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})\right]\phi_{i\sigma}(\mathbf{r}) = \epsilon^{\mathrm{KS}}_{i\sigma}\phi_{i\sigma}(\mathbf{r}). \tag{7}$$

All electron-electron interactions beyond the Hartree mean field are encompassed by the exchange-correlation potential v_{xc}, which is formally given as the functional derivative of the exchange-correlation energy E_{xc}:

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad . \tag{8}$$

In analogy to the quasiparticle equation (1) the Kohn-Sham eigenvalues $\epsilon^{\mathrm{KS}}_{i\sigma}$ are often interpreted as excitation energies, although this is not formally justified.

One of the most common approximations for E_{xc} is the local-density approximation (LDA) [10], in which the many-body exchange and correlation contributions to the total energy (E_{xc}) are included by comparison with the homogeneous electron gas (HEG):

$$E^{\mathrm{LDA}}_{xc}[n] = \int d\mathbf{r}\, n(\mathbf{r})\epsilon^{\mathrm{HEG}}_{xc}[n(\mathbf{r})] \quad . \tag{9}$$

Here [12] we follow the parameterization of Perdew and Zunger [13] for the exchange-correlation energy density $\epsilon^{\mathrm{HEG}}_{xc}[n(\mathbf{r})]$ of the homogeneous electron gas based on the data of Ceperley and Alder [14].

The LDA has been remarkably successful at accounting for correlation even in systems that are highly inhomogeneous. However, it is well known that the introduction of correlation in the LDA comes at the expense of the exact treatment of the self-interaction. Because the exchange functional is taken from the homogeneous electron gas it no-longer cancels the spurious self-interaction present in the Hartree term. In most systems this is a minor effect and is more than compensated by the improved treatment of the electron correlation. The LDA can be improved by explicitly removing the self-interaction [13], however this becomes increasingly difficult as the system's complexity is increased.

III. THE *GW* APPROXIMATION

In Hedin's GW approximation [1] the self-energy in Eq. 2 is given by

$$\Sigma_{\sigma\sigma}(\mathbf{r},\mathbf{r}';\epsilon) = \frac{i}{2\pi}\int_{-\infty}^{\infty} d\epsilon' e^{i\epsilon'\delta} G_{\sigma\sigma}(\mathbf{r},\mathbf{r}';\epsilon+\epsilon')W(\mathbf{r},\mathbf{r}';\epsilon) \tag{10}$$

where δ is an infinitesimal positive time. At the level of GW, spin flips are not accounted for [2], and the input Green's function is diagonal in its spin representation $G_{\sigma\sigma} = G_{\sigma\sigma'}\delta_{\sigma\sigma'}$

In common with usual GW calculations, a Kohn-Sham Green's function G^0 is used for G, given by [15]

$$G^0_{\sigma\sigma}(\mathbf{r},\mathbf{r}',\epsilon) = \sum_i \frac{\phi_{i\sigma}(\mathbf{r})\phi^*_{i\sigma}(\mathbf{r}')}{\epsilon - \epsilon^{\mathrm{KS}}_{i\sigma} \mp i\delta}, \tag{11}$$

and makes the non-interacting polarizability

$$\chi^0_{\sigma\sigma}(\mathbf{r},\mathbf{r}',\epsilon) = -\frac{i}{\pi}\int_{-\infty}^{\infty} d\epsilon' G^0_{\sigma\sigma}(\mathbf{r},\mathbf{r}';\epsilon'-\epsilon)G^0_{\sigma\sigma}(\mathbf{r}',\mathbf{r};\epsilon') \tag{12}$$

and the dielectric function spin-dependent (though spin-diagonal). The inverse dielectric function in the random-phase approximation

$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\epsilon) = \left[\delta(\mathbf{r}-\mathbf{r}') - \int d\mathbf{r}'' v(\mathbf{r},\mathbf{r}'') \sum_{\sigma} \chi^0_{\sigma\sigma}(\mathbf{r}'',\mathbf{r}',\epsilon)\right]^{-1} \tag{13}$$

and thus the screened Coulomb interaction

$$W_0(\mathbf{r},\mathbf{r}',\epsilon) = \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r},\mathbf{r}'',\epsilon) v(\mathbf{r}'',\mathbf{r}'). \tag{14}$$

then emerge as spin-independent quantities, giving rise to the simple spin dependence in the GW self-energy (Eq. 10).

For numerical convenience and physical insight we separate the GW self-energy (10) according to

$$\Sigma_{\sigma\sigma} = -i[G_{\sigma\sigma}v + G_{\sigma\sigma}(W-v)] = \Sigma^x_{\sigma\sigma} + \Sigma^c_{\sigma\sigma} \quad . \tag{15}$$

The first term ($\Sigma^x_{\sigma\sigma}$) corresponds to the Fock operator in Eq. 3 and will exactly cancel the self-interaction introduced by the Hartree potential. It is therefore immediately clear that any deviation from the exact result for hydrogen can only come from the correlation part of the self-energy ($\Sigma^c_{\sigma\sigma}$).

The incorrect self-interaction affects the electron removal energies (here, the ionization potential). For electron addition energies such as the electron affinity, the entire Hartree potential has a physically reasonable interpretation, since it acts on the wavefunction of the originally unoccupied state which has not contributed to the electron density.

IV. COMPUTATIONAL APPROACH

We solve the quasiparticle equation (1) with the G_0W_0 self-energy (10) for the quasiparticle energies and wavefunctions by fully diagonalizing the quasiparticle Hamiltonian in the basis of the single particle orbitals of the non-interacting system. Since the ground state of the hydrogen atom (Eq. 5) is spherically symmetric, it is sufficient to describe all non-local operators in the GW formalism by two radial and one spin coordinates, r, r', σ and one angular coordinate, θ, that denotes the angle between the vectors $\mathbf{r}$ and $\mathbf{r}'$. The self-energy (Eq. 10) then assumes the much simpler form

$$\Sigma_{\sigma\sigma}(r,r',\theta;\omega) = \sum_{l=0}^{\infty} [\Sigma_{l\sigma}(r,r';\omega)]\, P_l(\cos\theta)\delta_{\sigma,\sigma} \tag{16}$$

where $P_l(\cos\theta)$ is a Legendre polynomial of order l.

The Legendre expansion coefficients of the self-energy are calculated directly, thereby surpassing the need for a numerical treatment of the angular dependence. We use a real-space and imaginary time representation [16] to calculate the self-energy from the non-interacting Green's function G_0. The expression for the self-energy on the real frequency axis is obtained by analytic continuation [16]. The current implementation has been successfully applied to jellium clusters [17] and light atoms [7].

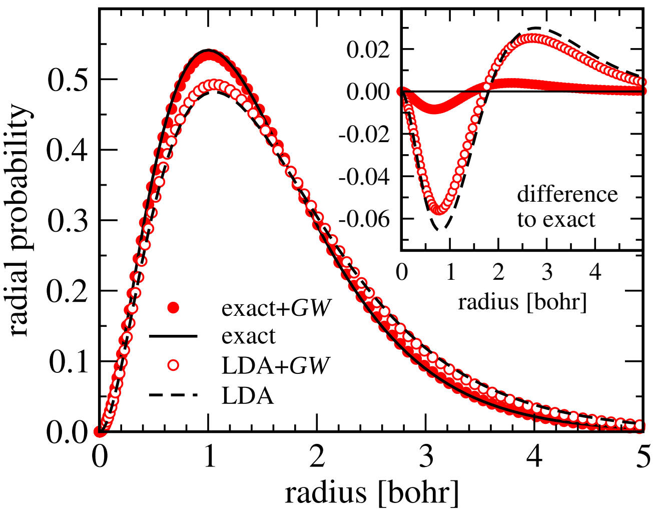

FIG. 1: Radial probability distributions of the hydrogen 1s state: the quasiparticle wavefunction deviates only slightly from the exact wavefunction, when the latter is used as a starting point (exact+GW). The LDA wavefunction, on the other hand, is more delocalized as a result of the inherent self-interaction. Adding quasiparticle corrections (LDA+GW) brings the resulting quasiparticle wavefunction slightly closer to the exact one again. The inset shows the difference to the exact wavefunction.

Our code allows us to solve the quasiparticle equation (1) for the GW self-energy with no further approximation. However, in order to separate the contribution that arises from the correlation part of the self-energy from that of the exchange part and the Hartree and exchange-correlation potential we *also* solve the quasiparticle equation with the frequently made approximation that the quasiparticle wavefunctions are given by the Kohn-Sham wavefunctions. The resulting equation for the quasiparticle energies is

$$\epsilon^{qp}_{i\sigma} = \epsilon^{\mathrm{KS}}_{i\sigma} + \langle \Sigma^x_{\sigma\sigma} \rangle + \langle \Sigma^c_{\sigma\sigma}(\epsilon^{qp}_{i\sigma}) \rangle - \langle v^{xc}_{\sigma} \rangle, \tag{17}$$

where the brackets $\langle\rangle$ denote matrix elements with respect to the Kohn-Sham wavefunction $\phi_{i\sigma}$.

In order to explore the role of the starting points for a GW calculation, two possible Kohn-Sham input Green's functions are chosen. First, the familiar LDA, and, second, the exact Kohn-Sham solution for the hydrogen atom which has the exact wavefunction of the hydrogen 1s state (5) and $v_{xc}(\mathbf{r}) = -v_H(\mathbf{r})$. (This exact Kohn-Sham Green's function, incidentally, differs from the exact Green's function of the hydrogen atom, because the exact Kohn-Sham unoccupied eigenvalues do not signify electron affinities. The exact Green's function cannot be constructed from any orthonormal set of one-particle wavefunctions.)

Exact	HF	LDA	LDA+GW	Exact+GW
-13.61	-13.61	-6.36	-12.66	-13.40

TABLE I: Quasiparticle energies (eV) for the $1s$ state of hydrogen (the ionization potential) obtained by diagonalizing the quasiparticle Hamiltonian (1). Two GW calculations are shown, starting from the LDA and from exact Kohn-Sham, respectively. For comparison, the Hartree-Fock (HF) and LDA eigenvalues are also shown.

Kohn-Sham G_0	ϵ_{1s}^{GW}	$\langle\Sigma_x\rangle$	$\langle v_{xc}\rangle$	$\langle\Sigma_c\rangle$
LDA	-12.93	-15.38	-8.25	0.56
Exact	-13.35	-17.00	-17.00	0.25

TABLE II: Quasiparticle energies (eV) for the $1s$ state of hydrogen obtained by solving Eq. (17). The contributions from the exchange $\langle\Sigma_x\rangle$ and correlation $\langle\Sigma_c\rangle$ part of the self-energy are compared to that of the exchange-correlation potential $\langle v_{xc}\rangle$ for the LDA and the exact case ($v_{xc} = -v_H$) as a starting point. Exact value for ϵ_{1s} is -13.61 eV.

V. RESULTS AND DISCUSSION

The calculated ionization potentials (from a full solution of the quasiparticle equation) are shown in Table I. The self-interaction errors in the two GW quasiparticle energies are seen to be fairly small: 0.95 eV when the approximate LDA Kohn-Sham starting point is used, and the much smaller 0.21 eV when the exact Kohn-Sham starting point is used. Clearly the LDA is such a physically poor representation of the correct physics in this extreme system (owing to the large self-interaction present in the LDA calculation itself, as reflected in the large error in the LDA Kohn-Sham eigenvalue) that it forms a very unsuitable starting point for GW. However, a physically reasonable starting point reduces the GW self-interaction error to a small size.

Since $\langle\Sigma_c\rangle$ gives a non-vanishing contribution to the hydrogen $1s$ state, even if the analytic solution is used as a starting point, the quasiparticle wavefunction will differ from the exact one. Figure 1 shows that the GW correlation gives rise to a slight delocalization of the quasiparticle wavefunction in this case. This relaxation, however, now makes the quasiparticle wavefunction an eigenfunction of the quasiparticle Hamiltonian and reduces the deviation from the exact energy of the $1s$ state to 0.2 eV, as shown in Table I. In the LDA the self-interaction error is much more pronounced and the wavefunction becomes significantly more delocalized. The GW self-energy corrects this to a small extent (as reflected in the quasiparticle wavefunction), but the remaining discrepancy reiterates the unsuitability of the LDA as a starting point for GW in this self-interaction-dominated atom.

For an analysis of the contributions to the self-energy we turn to the perturbative solution of the quasiparticle equation using Eq. 17, shown in Table II. When the exact Kohn-Sham wavefunction and eigenvalues are used, as in the Hartree-Fock case the exchange part of the self-energy is seen to cancel the self-interaction contribution from the Hartree potential exactly. The correlation part, on the other hand, is not zero, but amounts to a self-polarization of 0.25 eV. When the LDA is used as starting point the influence of the LDA wavefunction on the exchange operator becomes apparent and it reduces from -17.00 eV in the exact case to -15.38 eV. This corrects the highly overestimated LDA eigenvalue for the $1s$ state of -6.36 eV (see Table I) to -13.49 eV. However, in this case the contribution from the correlation part of the GW self-energy is even larger than when starting from the exact case and increases the quasiparticle energy to -12.93 eV.

VI. CONCLUSION

We have performed spin-resolved benchmark calculations for the GW formalism using the analytically known solutions of the hydrogen atom as a reference, making the self-interaction error introduced by the correlation part of the GW self-energy directly assessable. When the exact Kohn-Sham Green's function is used as the input to GW, the self-interaction error is small (0.21 eV, one-thirtieth the size of that in the LDA), but not negligible. If the LDA Kohn-Sham Green's function is used, as done in many GW calculations for more complex systems, a larger self-interaction error remains, inherited from the LDA starting point.

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