Self-Consistent Solution of Dyson's Equation Up to Second Order for Closed- and Open-Shell Atomic Systems

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ABSTRACT: Green's function techniques offer new methods based upon perturbation theory to study many-body systems. The computational cost in these schemes is substantially higher than in density functional theory (DFT), but they offer a clear picture of the nature of correlations included in the calculations. In this way, a connection between the Green's function scheme and DFT can learn more about the underlying mechanisms of the latter. Therefore, we need the correlated density of some carefully selected systems. In this work, a numerical scheme is presented to solve the Dyson equation up to second order self-consistently for a few closed-shell (He, Be, Ne, Mg, and Ar) and open-shell (B, C, N, O, and F) atoms in coordinate space. A detailed discussion is held on the reproduction of total binding energies, ionization energies, electron affinities, and spectral strength distributions. Int J Quantum Chem 91: 113–118, 2003

Key words: Green's function scheme; Dyson's equation; density functional theory; many-body systems; closed- and open-shell systems

Introduction

Green's function techniques are powerful tools to study many-body systems in a diagrammatic way. The central equation in this method is the Dyson equation, which determines the Green's function of the system. To describe the interactions in the system, Dyson's equation uses an energy-dependent potential: the so-called self-energy. It is in general a complex and (in coordinate space) nonlocal quantity, which can be evaluated order by order in the interaction. The order of truncation is also the order up to which Dyson's equation is solved.

Because of the amount of information on the many-particle system included in the self-energy, many efforts have been invoked to solve Dyson's equation. While early attempts needed to reduce the numerical efforts substantially, present computer technology allows for a more advanced approach. In this way, we can study correlation effects in atomic systems on a self-consistent basis. The

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goal of this article is to outline a numerical scheme to solve Dyson's equation up to second order for nonrelativistic closed- and open-shell systems. As case studies, we took He, Be, Ne, Mg, and Ar for the closed-shell atoms, while for the open-shell group B, C, N, O, and F were taken.

The structure of the article is as follows: First, a survey will be given of the formalism and the numerical scheme used to solve Dyson's equation. The next section will cover some results. We restrict ourselves to a discussion of the total binding energy, the ionization energy, and the spectral strength distribution. For the open-shell atoms, some attention will be devoted to the electron affinity as well. The predictions are compared with experiment and other computational calculations. In the last section, a summary of the advantages of the scheme is presented along with a suggestion for future work.

Methods

In this section, we give an overview of the algorithm to solve Dyson's equation up to second order. Details on the formalism and the scheme can be found in Refs. [1] and [2].

The second-order Dyson equation for the single-particle (s.p.) Green's function in energy space is given by

$$[G^{(2)}(E)] = [G^{\mathrm{HF}}(E)] + [G^{\mathrm{HF}}(E)][\Sigma^{(2)}(E)][G^{(2)}(E)], \quad (1)$$

where G^{HF} is the Hartree–Fock (HF) approximation to the Green's function and $\Sigma^{(2)}(E)$ is the second-order term of the expansion of the self-energy in the two-body interaction V. The diagrammatic representation of the second-order Dyson equation is depicted in Figure 1. The wavy line involves a full antisymmeterization of the interaction and makes that the exchange diagrams are included in all diagrams presented in Figure 1. The corresponding analytic form for the second-order self-energy is derived according to the Feynman rules and reads (in a.u., where $\hbar = 1$)

$$\Sigma^{(2)}_{\alpha\beta}(E) = \frac{1}{(2\pi)^2} \sum_{\substack{\gamma_1,\gamma_2,\gamma_3\\ \gamma_4,\gamma_5,\gamma_6}} \frac{1}{2} \langle\alpha\gamma_6|V|\gamma_1\gamma_3\rangle_{as}\langle\gamma_2\gamma_4|V|\beta\gamma_5\rangle_{as} \times \int dE_1 \int dE_2 G_{\gamma_1\gamma_2}(E - E_1 + E_2) \times G_{\gamma_3\gamma_4}(E_1)G_{\gamma_5\gamma_6}(E_2). \quad (2)$$

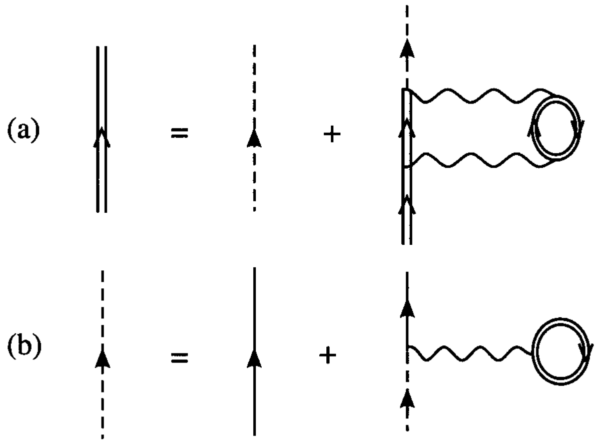

FIGURE 1. Second-order Dyson equation.

Here, the Greek letters include all quantum numbers necessary to specify a wave function in the chosen basis set. To determine the second-order propagator $G^{(2)}(E)$, first its HF approximation is to be calculated. As a result, the algorithm to tackle Dyson's second-order equation consists of two parts.

It is our intention to solve the first-order approximation of Dyson's equation (i.e., the HF equation) as much as possible in coordinate space to get the utmost accuracy, which is not guaranteed in finite basis sets. To achieve this goal, we start with solving the HF equations on a radial grid in coordinate space for the bound states only. In the second-order scheme, we also need to determine virtual orbitals located in the continuum part of the energy spectrum. An exact treatment of the continuum states in coordinate space is prohibitive. Therefore, we introduce some discretization scheme by adding a parabolic confining potential wall that starts at some appropriate distance from the nucleus. By the presence of this wall, the virtual levels become bound states and in a similar way as for the occupied states we can construct a complete and orthonormal set of eigenfunctions by solving the HF equations in coordinate space. Finally, we truncate this set without losing the completeness of the basis by some mechanism as outlined in Ref. [1].

To minimize the unphysical effects of the potential wall, we use this (quasi-) complete basis set to construct a matrix representation of the HF Hamiltonian without a wall. After diagonalization of the HF matrix, a new set of eigenfunctions is obtained that is also complete and not affected by the wall. This set is then kept fixed and used throughout the second stage of the calculation.

The second-order algorithm is computationally far more demanding than the first-order HF calculation. Therefore, to reduce the numerical effort we assumed that the s.p. propagator and self-energy are diagonal in the obtained HF basis set. This means that mixing between shells is not included in our model. This approximation turns out to give only a minor effects on the results.

Using the diagonal and discrete representation, the second-order Green's function can be written as a sum of simple energy poles,

$$G_{\alpha}^{(2)}(E) = \sum_{j} \frac{S_{\alpha,j}^{f}}{E - \epsilon_{\alpha,j}^{f} + i\eta} + \sum_{j} \frac{S_{\alpha,j}^{b}}{E - \epsilon_{\alpha,j}^{b} - i\eta}, \quad (3)$$

where the summation index j is restricted to the $(N \pm 1)$-electron states that can be reached from the N-electron atom by adding or removing an electron in orbital α (η is an infinitesimal convergence parameter).

For the self-consistent solution of Dyson's equation, we use the following iterative scheme:

- In the first iteration, the self-energy $\Sigma_{a}^{(2)[1]}$ is constructed using Eq. (2) and replacing the Green's functions by their HF estimates.
- The Green's function $G_{a}^{(2)[n]}(E)$ of the next iteration is evaluated through Eq. (1)

  $$G_{\alpha}^{(2)[n]}(E) = \frac{1}{E - \epsilon_{\alpha}^{\mathrm{HF}[n-1]} - \Sigma_{\alpha}^{(2)[n-1]}(E)}, \quad n = 2, 3 \ldots, \quad (4)$$

  where $\epsilon_{\alpha}^{\mathrm{HF}[n-1]}$ is the HF energy of orbital α in the preceding iteration. From this equation the poles and residues (also called spectroscopic factors) needed in Eq. (3) can be obtained, yielding a new estimate for the second-order Green's function. The second-order self-energy in the nth iteration, $\Sigma_{\alpha}^{(2)[n]}(E)$, is evaluated, through Eq. (2), with the nth iteration Green's function $G_{\alpha}^{(2)[n]}(E)$.
- The procedure is repeated until convergence is reached.

The above scheme was implemented in Ref. [1] for a series of spin-saturated closed-shell atoms, in which the single-particle states can be labeled with spherical quantum numbers independent of spin. The extension presented in Ref. [2] deals with a series of open-shell atoms having a partially filled 2p-shell. In this case, we must allow different spin orbitals for the two spin species. We can, however, retain spherical quantum numbers by taking suitable angular averages. Dominant spatial polarization effects are included by considering two different types of $l = 1$ spin orbitals. The net result is that the number of single-particle states is roughly doubled as compared to a closed-shell atom, with a corresponding increase in the numerical effort.

Results and Discussion

Now we present some results of the Dyson(1) and Dyson(2) calculations. They are compared with experiment and other computational schemes (standard HF, post-HF methods, DFT-BLYP, and DFT-B3LYP) performed with the Gaussian 98 package. In Table I, we report the HF single-particle energies of the highest occupied bound level. If rearrangement effects in the $(A - 1)$ system are not taken into account in the mean field due to the removal of an electron, these s.p. energies may be regarded as ionization energies. Koopman's theorem is almost valid for HF s.p. levels but not for Kohn–Sham (KS) levels, as clearly demonstrated by the poor DFT results (first two columns in Table I). However, a more adequate definition of the ionization energy is given by the difference in binding energy of the $(A - 1)$ and A-particle system. Now, we notice a remarkable agreement between the DFT results and the experimental estimates, emphasizing the semiempirical nature of the DFT functionals and the inclusion of these atoms in the training set. The HF predictions are reasonable but obviously do not involve sufficient correlations for a more stringent agreement. The Dyson(2) estimates substantially improve the final results, and the trend in the good direction is already set from the first iteration.

The open-shell systems also offer the opportunity to study the electron affinity (Table II), where correlations are in general believed to be extremely important. This is clearly demonstrated by the HF results, which fail in reproducing even the qualitative trend of the binding energies of the $(A + 1)$ system vs. A-particle system. The first two columns of Table II give the electron affinities as obtained in DFT calculations using standard functionals. We also add into the table extended ab initio calculations with inclusion of various correction terms [4]. Their predicted theoretical values are the best available in the literature, but are not completely self-consistent and not free from any empirical input.

TABLE I
First ionization energies for some atomic systems (a.u.).

	DFT				HF		Dyson(2)			
	$-3x/\epsilon_\alpha^{\mathrm{KS}}$		$E_0(A) - E_0(A - 1)$		$-3x/\epsilon_\alpha^{\mathrm{HF}}$		$-3x/\epsilon_\alpha$			
	BLYP	B3LYP	BLYP	B3LYP	HF/6-311g**	Dyson(1)	First it.	Second it.	Conv.	Exp.[a]
He	0.578	0.658	0.911	0.916	0.917	0.918	0.905	0.906	0.906	0.9036
Be	0.200	0.231	0.330	0.335	0.309	0.309	0.330	0.318	0.320	0.3426
B	0.143	0.187	0.316	0.321	0.317	0.311	0.308	0.304	0.305	0.3049
C	0.211	0.264	0.417	0.424	0.437	0.435	0.417	0.415	0.415	0.41381
N	0.286	0.352	0.532	0.538	0.568	0.571	0.534	0.535	0.537	0.53412
O	0.256	0.324	0.514	0.516	0.516	0.510	0.480	0.483	0.484	0.50045
F	0.353	0.431	0.643	0.647	0.673	0.674	0.608	0.616	0.618	0.64028
Ne	0.460	0.550	0.796	0.793	0.842	0.850	0.745	0.758	0.763	0.79248
Mg	0.168	0.194	0.280	0.284	0.253	0.253	0.276	0.272	0.274	0.2810
Ar	0.370	0.427	0.576	0.582	0.590	0.590	0.578	0.581	0.585	0.5792

Dyson(1) stands for HF in coordinate space. Dyson(2) gives the solution of Dyson's equation in second order after one and two iterations and after convergence.

[a] Ref. [3].

As already mentioned, the Dyson(1) predictions for the electron affinities do not conform to the experimental findings, and it is likely that the Dyson(1) results differ in a substantial way from exact HF values for the affinities defined as $E_0(A) - E_0(A + 1)$. As opposed to HF, the Dyson(2) results are spectacular. Full convergence is required to produce electron affinities in close agreement with experiment. It supports the assumption that the electron correlations built into the "dressed" second-order self-energy diagram are playing an important role and are in some cases sufficient for reproducing correlation-sensitive quantities such as electron affinities. The first iteration results vary significantly from the convergent values, indicating the complex nature of the electron correlations reflected in complicated high-order diagrams in the self-energy constructed with HF propagators. For the nitrogen atom the electron affinity remains negative, in complete agreement with experiment that no stable negative nitrogen atom can be found (see, e.g., [11]). The residues of the poles of the Dyson(2) Green's function stand for the spectroscopic factors of the s.p. state under consideration. The correlations incorporated in the self-energy of the Dyson(2) self-consistent scheme are responsible for a spreading of the spectroscopic strength over a wide energy region. We demonstrate this fragmen-

TABLE II
Electron affinities for some atomic systems (a.u.).

	DFT		SCF + CCSDT	HF		Dyson(2)			
	$E_0(A) - E_0(A + 1)$		+corr [4]	Dyson(1)	HF/6-311g**	$-\epsilon_\alpha$			
	BLYP	B3LYP	$E_0(A) - E_0(A + 1)$	$-\epsilon_\alpha^{\mathrm{HF}}$	$E_0(A) - E_0(A + 1)$	First it.	Second it.	Conv.	Exp.
B	−0.0165	−0.0102	0.01024	−0.0358	−0.030	−0.003	0.006	0.008	0.010279 (64)[a]
C	0.0145	0.0202	0.04641	−0.0198	−0.002	0.033	0.045	0.046	0.046382 (0)[b]
N	−0.0470	−0.0438	—	−0.1080	−0.109	−0.0491	−0.039	−0.039	<0
O	0.0012	0.0057	0.05368	−0.0792	−0.060	0.014	0.032	0.032	0.053695 (3)[c]
F	0.0642	0.0675	0.12505	−0.0369	0.006	0.098	0.126	0.126	0.124991 (5)[d]

See Table I caption.

[a] Ref. [5].

[b] Ref. [6].

[c] Ref. [3].

[d] Ref. [3].

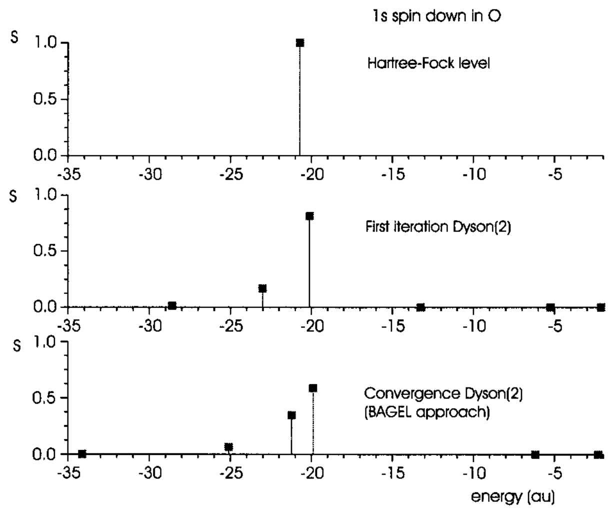

FIGURE 2. Spectroscopic factor of 1*s* ↓ in O as predicted in the Dyson(1) and Dyson(2) scheme.

tation process in Figure 2 for the 1*s* ↓ level in the oxygen atom. Already from the first iteration the spectral strength is scattered over a large energy range and the main fragment is pushed to some higher energy. The effect of self-consistency is mainly to regroup the strength into some well-defined poles and further deplete the quasiparticle peak.

Table III gives an overview of various predictions of the total binding energy of the closed-shell systems in the ground state. The Dyson(1) value can be regarded as the limit of all HF results using finite basis sets. Perturbative schemes beyond HF involve additional correlations, achieving a better agreement with experiment and, as could be expected, configuration interaction (CI) determines the limit for this class of post-HF perturbation schemes. Involving more correlations by definition, Dyson(2) is obviously superior for all atomic systems under consideration. Only the DFT results can rival the Green's function method in describing the total binding energy, but their success can be attributed to the essentially empirical character of functionals [8–10].

The present self-consistent Green's function calculations lead to a considerable improvement in the total energy. A similar conclusion was reached in other electronic systems, e.g., the electron gas [12] or periodic solids [13], and recently attributed to the variational nature of the total energy in self-consistent calculations [14]. However, it was also found that full self-consistency (at the GW level) can lead to a worse description of spectral properties like the quasiparticle bandwidth as compared to partial or non-self-consistency. In this case, one probably needs a higher-level description of the interplay between single-particle propagation and the collec-

TABLE III

Total ground-state energy (a.u.) for closed-shell systems obtained with various many-body models.

	He	Be	Ne	Mg	Ar
DFT					
DFT-BLYP	−2.905	−14.659	−128.940	−200.081	−527.534
DFT-B3LYP	−2.913	−14.671	−128.951	−200.093	−527.553
HF					
HF/6-311g**	−2.860	−14.572	−128.523	−199.607	−526.807
Dyson(1)	−2.862	−14.573	−128.549	−199.617	−526.826
Post-HF					
MP2	−2.885	−14.599	−128.732	−199.629	−526.954
MP4(SDTQ)	−2.890	−14.613	−128.736	−199.638	−526.967
CI					
QCISD	−2.891	−14.617	−128.733	−199.635	−526.807
Dyson(2)					
First it.	−2.899	−14.633	−128.709	−199.751	−527.075
Second it.	−2.899	−14.631	−128.882	−199.944	−527.421
Conv.	−2.899	−14.628	−128.888	−199.948	−527.422
Exp.[a]	−2.904	−14.667	−128.928	−200.043	−527.549

In MP4, calculations with double-quadruple (DQ), single-double-quadruple (SDQ), and single-double-triple-quadruple (SDTQ) substitutions in the ground-state Slater determinant are considered.

[a] Ref. [7].

tive plasmon excitations. For the atomic systems under consideration in this article, the information on spectral strength distributions is not so detailed as to allow strong conclusions. For the quasiparticle strength of valence hole states, the difference between the first iteration result Z_0 (performed with HF propagators) and the converged result Z_c is modest, e.g., for the case of Ne we find $Z_0 = 0.885$ and $Z_c = 0.876$ for the 2*s* orbital, and $Z_0 = 0.909$ and $Z_c = 0.904$ for the 2*p* orbital, compared with experimental values $Z_{ex}(2s) = 0.85 \pm 0.02$ and $Z_{ex}(2p) = 0.92 \pm 0.02$ [15]. As seen from the first iteration and converged results in Table III, the requirement of self-consistency is beneficial for the total energy, with the exception of Be. A future extension of our scheme will include intershell mixing, the neglect of which is possibly not a good approximation for the strongly correlated Be atom.

Conclusion

In summary, we presented a computational scheme to solve Dyson's equation up to second order in a self-consistent way and that may be applied to closed- and open-shell atomic systems as well. The algorithm consists of two parts. First, the HF problem is solved on a radial grid in coordinate space. A discretization of the basis set is proposed that guarantees the completeness of the continuum and is used to tackle Dyson's equation in second order.

This scheme is applied to closed-shell atoms (He, Be, Ne, Mg, and Ar) and to the open-shell group B, C, N, O, and F. Single-particle observables such as total energy, ionization energy, electron affinity, and spectral strength distribution are discussed. These high-level results are compared with those obtained in other computational tools based on HF and DFT concepts but developed in finite basis sets. The role of electron correlations on these s.p. quantities is largely emphasized and their impact on these quantities is far from being negligible, yielding a remarkably better experimental agreement. This is the case in a spectacular way for the reproduction of the electron affinity in open-shell atomic systems, where the second-order effects turn out to be indispensable.

The key advantage of using the Green's function formalism is that the nature of the included correlations can be easily visualized by means of Feynman diagrams. The self-consistent Dyson(2) scheme is an ideal tool to learn more in a microscopic way about the mechanism of the correlations that are (to be) implemented in DFT functionals.

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