GW approximation with self-screening correction

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The GW approximation takes into account electrostatic self-interaction contained in the Hartree potential through the exchange potential. However, it has been known for a long time that the approximation contains self-screening error as evident in the case of the hydrogen atom. When applied to the hydrogen atom, the GW approximation does not yield the exact result for the electron removal spectra because of the presence of self-screening: the hole left behind is erroneously screened by the only electron in the system which is no longer present. We present a scheme to take into account self-screening and show that the removal of self-screening is equivalent to including exchange diagrams, as far as self-screening is concerned. The scheme is tested on a model hydrogen dimer and it is shown that the scheme yields the exact result to second order in \((U_0 - U_1)/2t\) where \(U_0\) and \(U_1\) are respectively the onsite and offsite Hubbard interaction parameters and \(t\) the hopping parameter.

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I. INTRODUCTION

In the Hartree approximation\textsuperscript{1}, a system of electrons move in a common potential arising from the electrostatic field of the electrons, in addition to the external field. In this approximation, a given electron experiences the electrostatic potential from the other electrons as well as from itself because the common potential or the Hartree potential contains the field from the electron itself. This unphysical self-interaction is removed when exchange interaction is included, leading to the Hartree-Fock approximation (HFA)\textsuperscript{2}. In density functional theory\textsuperscript{2}, Perdew and Zunger introduced the concept of self-interaction correction\textsuperscript{1} to remove a similar problem in the local density approximation (LDA).

For many-electron systems, such as solids, it is well known that the HFA is not satisfactory because it completely neglects screening which is very crucial in describing the electronic structure of many-electron systems. Thus, for example, the Hartree-Fock band gaps of semiconductors and insulators are much too wide and when the HFA is applied to metals the density of states at the Fermi level becomes unphysically zero due to the logarithmic singularity in the derivative of the one-particle energy with respect to the \(k\)-vector at \(k = k_F\).\textsuperscript{2} The simplest known and successful method beyond the HFA that cures the band-gap problem and the anomaly of the HFA in metals is the GW approximation (GWA)\textsuperscript{4,5}. The GWA includes the effects of frequency-dependent screening from first principles and the self-energy in space-time representation is approximated by a product of the Green function \(G\) and the screened interaction \(W\).

The GWA includes the exchange potential so that it is self-interaction free. However, it is contaminated by "self-screening", namely, an electron screens itself, analogous to "self-interaction" where an electron interacts with its own electrostatic field. This undesirable self-screening effect has been a long-standing problem and thought to be a source of significant errors in the electronic structure. The self-screening problem may be illustrated by the famous case of the hydrogen atom. Since there is only one electron, it is clear that the one-particle removal energy or the hole energy is simply given by 13.6 eV, the 1s orbital energy. The Hartree approximation applied to the hydrogen atom would yield a too low removal energy due to the self-interaction error while the HFA would give the correct result. Embarrassingly, when the GWA is applied to the hydrogen atom, it yields a wrong result because, as a consequence of self-screening, the correlation part of the hole self-energy in the GWA is not zero\textsuperscript{6}. Evidently, since there is only one electron, upon removal of the electron there are no other electrons that can screen the remaining hole so that the hole self-energy ought to be zero.

The self-screening error is believed to be responsible for a number of well-known problems. It has been suspected for a long time that the presence of self-screening in the GW self-energy may be responsible for errors in the quasiparticle energies of localized states. It has been found that GW quasiparticle energies of core or semicore states usually lie above the experimental values. It is argued that in the HFA the quasiparticle energies are too low due to the absence of screening and when screening is taken into account within the GWA, these energies are pushed up too high, an indication of overscreening due to self-screening. In molecules, a recent comprehensive and systematic study of 34 molecules has found that the GWA overscreens the Hartree-Fock ionization potential leading to underestimation by 0.4 ~ 0.5 eV compared to experiment\textsuperscript{8}. In many materials, the energy position of the core or semicore states is usually too high in the LDA due to self-interaction. GW calculations on the 3d
semicore states of a number of semiconductors such as GaAs and ZnSe improve the LDA results but the remaining error is still significant. It is very likely that this error owes its origin from self-screening. From physical consideration the self-screening error is expected to be significant when the states are rather localized but less important in extended states.

In this paper, we develop a new scheme which aims at correcting the self-screening error in the GW self-energy as well as the linear density-density response function within the random-phase approximation (RPA). An interesting consequence of the proposed scheme is the fact that the screened interaction $W$ becomes explicitly spin dependent, in contrast to the original GWA where the screened interaction is spin independent. We also furnish a theoretical support for the scheme by showing from diagrammatic consideration that the removal of the self-screening terms is partially equivalent to adding exchange diagrams. In other words, the self-screening terms are cancelled by corresponding terms in the exchange diagrams.

As an illustration of our scheme, we calculate the bonding-antibonding gap of a model hydrogen dimer. We have chosen this model because the exact result is known allowing for rigorous comparison. Moreover, the calculations can be performed analytically so that possible numerical errors are eliminated and the simplicity of the system permits us to analyze the results without unnecessary complicating factors. It is found that the self-screening corrected GWA reproduces the exact result to order $[(U_0 - U_1)/2t]^2$, where $U_0$ and $U_1$ are respectively the onsite and offsite Coulomb energies and $t$ is the hopping integral.

II. GW APPROXIMATION WITH SELF-SCREENING CORRECTION

A. Theory

The first step of the procedure is to decompose the non-interacting Green function into its orbital components:

$$G^{0}_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_{n} g_{n\sigma}(\mathbf{r}, \mathbf{r}'; \omega),$$  

$$g_{n\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\varphi_{n\sigma}(\mathbf{r})\varphi^{*}_{n\sigma}(\mathbf{r}')}{\omega - \varepsilon_{n\sigma}},$$  

where $h\varphi_{n\sigma} = \varepsilon_{n\sigma}\varphi_{n\sigma}$,

$$\Sigma_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = iG^{0}_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega)W(\mathbf{r}', \mathbf{r}) = i \sum_{m} g_{m\sigma}(\mathbf{r}, \mathbf{r}'; \omega)W(\mathbf{r}', \mathbf{r}; \mathbf{r}),$$  

where $W$ is the screened interaction

$$W = \epsilon^{-1}v$$  

with $\epsilon$ being the dielectric matrix.

Consider an electron occupying an orbital $\varphi_{m\sigma}$ propagating from $(\mathbf{r}'\mathbf{r})$ to $(\mathbf{r}\mathbf{r})$ represented by $g_{m\sigma}$. Another electron with the same spin cannot occupy the orbital $\varphi_{m\sigma}$ and therefore $g_{m\sigma}$ should not participate in the screening process during the propagation of the electron. Therefore the screened interaction $W$ should be calculated using a polarization propagator that does not include $g_{m\sigma}$. However, an electron in the same orbital but with opposite spin can naturally participate in the screening process. The self-energy then takes the following form:

$$\Sigma_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = i \sum_{m} g_{m\sigma}(\mathbf{r}, \mathbf{r}'; \omega)W_{m\sigma}(\mathbf{r}', \mathbf{r}),$$  

where

$$W_{m\sigma} = v + vR_{m\sigma}v = v + W^{c}_{m\sigma},$$  

$$R_{m\sigma} = P_{m\sigma} + P_{m\sigma}vR_{m\sigma}. $$  

The polarization $P_{m\sigma}$ is defined as the polarization without $g_{m\sigma}$, i.e., no Green function line in $P_{m\sigma}$ contains $g_{m\sigma}$. In other words,

$$P_{m\sigma} = -i(G_{m\sigma}G_{m\sigma} + G_{-\sigma}G_{-\sigma}),$$  

where $G_{m\sigma}$ is the Green function without $g_{m\sigma}$, namely,

$$G_{m\sigma} = G_{\sigma} - g_{m\sigma}. $$  

In Fig. 1 the self-energy diagrams corresponding to are compared with the conventional GW diagrams.

The correlation part of the GW self-energy with self-screening correction is given by

$$\Sigma^{c}_{\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = i \sum_{m} \int \frac{d\omega'}{2\pi} g_{m\sigma}(\mathbf{r}, \mathbf{r}'; \omega')W^{c}_{m\sigma}(\mathbf{r}', \mathbf{r})$$  

$$= i \sum_{m} \int \frac{d\omega'}{2\pi} \varphi_{m\sigma}(\mathbf{r})\varphi^{*}_{m\sigma}(\mathbf{r}')W^{c}_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega')$$  

$$= i \sum_{m} \int \frac{d\omega'}{2\pi} \varphi_{m\sigma}(\mathbf{r})\varphi^{*}_{m\sigma}(\mathbf{r}')W_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega') $$  

$$+ i \sum_{m} \int \frac{d\omega'}{2\pi} \varphi_{m\sigma}(\mathbf{r})\varphi^{*}_{m\sigma}(\mathbf{r}')W_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega'),$$  

$$= i \sum_{m} \int \frac{d\omega'}{2\pi} \varphi_{m\sigma}(\mathbf{r})\varphi^{*}_{m\sigma}(\mathbf{r}')W_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega') $$
Writing the correlation part of the screened interaction, $W^c$, in its spectral representation

\[
W^c_{m\sigma}(r', r; \omega') = \int_{-\infty}^{0} d\omega'' D_{m\sigma}(r', r; \omega'') \frac{\omega - \omega'' - i\delta}{\omega'' - \omega'} + \int_{0}^{\infty} d\omega'' D_{m\sigma}(r', r; \omega'') \frac{\omega - \omega'' + i\delta}{\omega'' - \omega'},
\]

(12)

the frequency integral over $\omega'$ can be performed analytically. The correlation part of the self-energy may be divided into two parts, $\Sigma^{occ}$ and $\Sigma^{unocc}$:

\[
\Sigma^{occ}(r, r'; \omega) = \sum_{m} \int_{0}^{\infty} d\omega'' \frac{\varphi_{m\sigma}(r)D_{m\sigma}(r', r; \omega'')\varphi^*_{m\sigma}(r')}{\omega + \omega'' - \varepsilon_{m\sigma} - i\delta},
\]

(13)  \[
\Sigma^{unocc}_{\alpha}(r, r'; \omega) = \sum_{m} \int_{0}^{\infty} d\omega'' \frac{\varphi_{m\sigma}(r)D_{m\sigma}(r', r; \omega'')\varphi^*_{m\sigma}(r')}{\omega - \omega'' - \varepsilon_{m\sigma} + i\delta},
\]

(14)

$D_{m\sigma}$ is the spectral function of $W^c_{m\sigma}$ and we have used the relations

\[
D_{m\sigma}(-\omega) = -D_{m\sigma}(\omega), \quad W^c_{m\sigma}(-\omega) = W^c_{m\sigma}(\omega)
\]

(15)  and

\[
D_{m\sigma}(\omega) = -\frac{1}{\pi} \text{Im} W^c_{m\sigma}(\omega) \text{sgn}(\omega).
\]

The corresponding expressions for the self-energy in the conventional GWA are the same as above except that $D_{m\sigma}$ is replaced by the spectral function of $W$ instead.

It is worth noting that the self-screening correction introduces spin dependence in the screened interaction $W$ as can be seen in (13). Each electron experiences a different screened interaction $W_{m\sigma}$ which is not only orbital dependent but also spin dependent according to the orbital occupied by the electron as well as the spin of the electron.

Since in the exact set of Hedin’s equations the screened interaction $W$ is spin independent the appearance of a spin-dependent screened interaction seems unnecessary. It is interesting to make comparison with density functional theory. In principle, the total energy is obtainable from the ground-state electron density, which is the sum of spin up and down components. In practice, for spin-polarized systems it is more favorable to introduce the spin variable and regard the total energy as a functional of the up and down spin densities. The separation of the density into the up and down components mimics the physical situation and thereby promotes a better self-energy within the simple GWA. If we kept the conventional screened interaction, we would need to include exchange diagrams as vertex corrections to cancel the self-screening terms, as shown in a later section. It is much simpler to remove the self-screening terms than to include vertex corrections.

**B. Self-screening correction in extended states**

For extended states, the self-screening correction tends to vanish. However, from the physical point of view, we expect that the self-screening correction is significant when the state originates from a localized orbital such as the case with the states originating from the 3d or 4f orbitals. Consider expanding a given Bloch state in its Wannier representation.

\[
\psi_{k\sigma}(r) = \frac{1}{\sqrt{N}} \sum_{R} \exp(i \mathbf{k} \cdot \mathbf{R}) \chi_{R\sigma}(r).
\]

(17)

The Green function is, with $\varepsilon_{k\sigma} \to \varepsilon_{k\sigma} + i\eta$ for occupied states and $\varepsilon_{k\sigma} \to \varepsilon_{k\sigma} - i\eta$ for unoccupied states,
\( G^0_\sigma(r, r'; \omega) \)
\( = \sum_{\mathbf{k}_n} \frac{\psi_{\mathbf{k}_n \sigma}(r) \psi_{\mathbf{k}_n \sigma}^*(r')}{\omega - \varepsilon_{\mathbf{k}_n \sigma}} \)
\( = \frac{1}{N} \sum_{\mathbf{k}_n} \sum_{\mathbf{R} \neq \mathbf{R}'} \frac{\exp[i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \chi_{\mathbf{R} \sigma}(r) \chi_{\mathbf{R} \sigma}^*(r')}{\omega - \varepsilon_{\mathbf{k}_n \sigma}} \)
\( = \frac{1}{N} \sum_{\mathbf{k}_n} \sum_{\mathbf{R} \neq \mathbf{R}'} \frac{\exp[i \mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \chi_{\mathbf{R} \sigma}(r) \chi_{\mathbf{R} \sigma}^*(r')}{\omega - \varepsilon_{\mathbf{k}_n \sigma}} \)
\( + \frac{1}{N} \sum_{\mathbf{k}_n} \chi_{\mathbf{R} \sigma}(r) \chi_{\mathbf{R} \sigma}^*(r') \), \hspace{1cm} (18)

We apply the self-screening correction to the component of \( G^0_\sigma \) corresponding to \( \mathbf{R} = \mathbf{R}' \). As before we define
\( g_{\sigma \sigma}(r, r'; \omega) = \frac{1}{N} \sum_{\mathbf{k}} \sum_{\mathbf{R}} \chi_{\mathbf{R} \sigma}(r) \chi_{\mathbf{R} \sigma}^*(r') \)
\( = \frac{1}{N} \sum_{\mathbf{R}} \chi_{\mathbf{R} \sigma}(r) g_{\sigma \sigma}(\omega) \chi_{\mathbf{R} \sigma}^*(r'), \) \hspace{1cm} (20)

where
\( g_{\sigma \sigma}(\omega) = \sum_{\mathbf{k}} \frac{1}{\omega - \varepsilon_{\mathbf{k} \sigma \sigma}}. \) \hspace{1cm} (21)

In practice, there may be a problem due to the non-analytic behaviour of \( \varepsilon_{\mathbf{k} \sigma \sigma} \) as a function of \( \mathbf{k} \). For very narrow band such as the one formed by semicore states we may make the following approximation
\( g_{\sigma \sigma}(r, r'; \omega) \approx \frac{1}{N} \sum_{\mathbf{R}} \frac{\chi_{\mathbf{R} \sigma}(r) \chi_{\mathbf{R} \sigma}^*(r')}{\omega - \varepsilon_{\mathbf{k} \sigma \sigma}} \) \hspace{1cm} (22)

\( \left\langle \varepsilon_{\sigma \sigma} \right\rangle = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k} \sigma \sigma}. \) \hspace{1cm} (23)

For a given site \( R \) the orbital Green function \( g_{\sigma \sigma} \) is confined to the site and it is equivalent to a core state Green function.

C. Theoretical justification of self-screening correction

Here we show that removing the self-screening terms in the self-energy is partially equivalent to adding vertex corrections in the form of exchange diagrams. It can be shown that the self-screening terms are cancelled by the corresponding terms in the exchange diagrams in a similar fashion as for the first-order self-energy or the HFA. We will illustrate the idea for the second-order self-energy but it is clear that the argument applies to any order. The second-order exchange and direct diagrams are shown in the upper part of Fig. 2.

According to the Feynman rules, the second-order exchange self-energy for a given spin is
\( \Sigma^x(x_1, x_2) = (i)^2 \int dx_3 dx_4 G(x_1, x_3) G(x_3, x_4) \times G(x_4, x_2) v(x_1 - x_4)v(x_3 - x_2), \) \hspace{1cm} (24)

where \( x = (r, t) \) and
\( v(x - x') = v(r - r') \delta(t - t'). \) \hspace{1cm} (25)

Fourier transformation with respect to \( \tau = t_1 - t_2 \) yields
\( \Sigma^x(r_1, r_2; \omega) = -\int d^3 r_3 d^3 r_4 \int \frac{d\omega_4 d\omega_2}{(2\pi)^2} G(r_1, r_3; \omega_1) \times G(r_3, r_4; \omega_2) G(r_4, r_2; \omega - \omega_1 + \omega_2) \times v(r_1 - r_4)v(r_2 - r_3). \) \hspace{1cm} (26)

Using a non-interacting Green function of a given spin
\( G^0(r, r'; \omega) = \sum_{\text{occ}} \frac{\varphi_n(r) \varphi_n^*(r')}{\omega - \varepsilon_n - i\delta} + \sum_{\text{unocc}} \frac{\varphi_m(r) \varphi_m^*(r')}{\omega - \varepsilon_m + i\delta}, \) \hspace{1cm} (27)

we can perform the frequency integral over \( \omega_2 \) using Cauchy’s theorem by closing the contour either in the upper or lower plane:
\( \int \frac{d\omega_2}{2\pi} G^0(r_3, r_4; \omega_2) G^0(r_1, r_2; \omega - \omega_1 + \omega_2) \)
\( = \int \sum_{\text{occ}} \sum_{\text{unocc}} \left\{ \frac{\varphi_n(r_3) \varphi_n^*(r_4) \varphi_m(r_4) \varphi_m^*(r_2)}{\omega - \omega_1 + \varepsilon_n - \varepsilon_m + i\delta} + \frac{\varphi_m(r_3) \varphi_m^*(r_4) \varphi_n(r_4) \varphi_n^*(r_2)}{\omega - \omega_1 + \varepsilon_m - \varepsilon_n - i\delta} \right\}. \) \hspace{1cm} (28)

![FIG. 2: The second-order exchange and direct self-energy and polarization diagrams. As shown in the text, the exchange diagrams cancel the self-screening terms in the direct diagrams.](image)
Similarly, integrating over \( \omega_1 \) we find

\[
\Sigma^x(r_1, r_2; \omega) = -\sum_{\text{occ}} \sum_{\text{unocc}} \int d^3 r_3 d^3 r_4 \ v(r_1 - r_4) v(r_3 - r_2) \\
	imes \left\{ \sum_k \frac{\varphi_k(r_1) \varphi_k^*(r_2) \varphi_m(r_3) \varphi_m^*(r_4) \varphi_n(r_4) \varphi_n^*(r_2)}{\omega - \varepsilon_k + \varepsilon_m - \varepsilon_n - i\delta} + \sum_k \frac{\varphi_k(r_1) \varphi_k^*(r_2) \varphi_n(r_3) \varphi_n^*(r_4) \varphi_m(r_4) \varphi_m^*(r_2)}{\omega - \varepsilon_k + \varepsilon_n - \varepsilon_m + i\delta} \right\}.
\]

(29)

The second-order direct self-energy is

\[
\Sigma^d(x_1, x_2) = -(i)^2 \int dx_3 dx_4 G(x_1, x_2) G(x_3, x_4) G(x_4, x_3) \\
\times v(x_1 - x_4) v(x_3 - x_2),
\]

(30)

and we have considered the direct term with all \( G \) having the same spin since this is the term that contains self-screening. Its Fourier transform is given by

\[
\Sigma^d(r_1, r_2; \omega) = \int d^3 r_3 d^3 r_4 \int \frac{d\omega_1 d\omega_2}{(2\pi)^2} \times G(r_1, r_2; \omega_1) \\
\times G(r_3, r_4; \omega_2) G(r_4, r_3; \omega - \omega_1 + \omega_2) \\
\times v(r_1 - r_4) v(r_3 - r_2),
\]

(31)

which can be calculated analytically as in the exchange case yielding

\[
\Sigma^d(r_1, r_2; \omega) = \sum_{\text{occ}} \sum_{\text{unocc}} \int d^3 r_3 d^3 r_4 \ v(r_1 - r_4) v(r_3 - r_2) \\
\times \left\{ \sum_k \frac{\varphi_k(r_1) \varphi_k^*(r_2) \varphi_m(r_3) \varphi_m^*(r_4) \varphi_n(r_4) \varphi_n^*(r_3)}{\omega - \varepsilon_k + \varepsilon_m - \varepsilon_n - i\delta} + \sum_k \frac{\varphi_k(r_1) \varphi_k^*(r_2) \varphi_n(r_3) \varphi_n^*(r_4) \varphi_m(r_4) \varphi_m^*(r_3)}{\omega - \varepsilon_k + \varepsilon_n - \varepsilon_m + i\delta} \right\}.
\]

(32)

Comparison between \( \Sigma^d \) and \( \Sigma^x \) reveals that the self-screening terms \( n = k \) in \( \Sigma^d \) for an occupied \( \varphi_k \),

\[
\frac{\varphi_k(r_1) \varphi_k^*(r_2) \varphi_m(r_3) \varphi_m^*(r_4) \varphi_n(r_4) \varphi_n^*(r_3)}{\omega - \varepsilon_k + \varepsilon_m - \varepsilon_n - i\delta},
\]

(33)

where \( \varphi_m \) is unoccupied, are cancelled by the corresponding terms in \( \Sigma^x \). Similarly for the case when \( \varphi_k \) is unoccupied. Thus we see that by removing the self-screening terms from the direct self-energy we effectively include the exchange self-energy.

III. THE RANDOM-PHASE APPROXIMATION WITH SELF-POLARIZATION CORRECTION

In the previous section we have developed a scheme for removing the self-screening in the random-phase approximation (RPA) in relation to the GW approximation. When considering the propagation of an electron or a hole that is screened by the surrounding electrons, the electron or hole in question should not participate in the screening process. Here, we apply an analogous idea to the case where the perturbation is not due to an electron or a hole but to a dipole or an electron-hole excitation.

In the RPA the polarization is given by

\[
P(r, r'; \omega) = \sum_\alpha \left\{ \frac{d_\alpha(r) d_\alpha^*(r')}{\omega - \Delta_\alpha} - \frac{d_\alpha(r') d_\alpha^*(r)}{\omega + \Delta_\alpha} \right\}
\]

(34)

\[
d_\alpha(r) = \varphi_m(r) \varphi_n^*(r),
\]

\[
\Delta_\alpha = \varepsilon_m - \varepsilon_n - i\delta, \quad \varepsilon_m > \mu, \quad \varepsilon_n \leq \mu.
\]

(35)

The index \( \alpha \) includes the spin. The response function is given by

\[
R = [1 - P v]^\dagger P
\]

\[
= P + P v P + P v P v P + \cdots.
\]

(36)

We can think of \( [1 - P v]^\dagger = \epsilon^{-1} \) as a screening factor that screens the bare polarization \( P \) which consists of electron-hole excitations \( \{p_\alpha\} \). We observe that a given electron-hole excitation \( p_\alpha \) generates via the Coulomb interaction screening polarizations that include itself because \( P \) contains \( p_\alpha \). To eliminate this self-polarization we therefore calculate the self-polarization corrected response function as follows:

\[
R = \sum_\alpha [1 - P_\alpha]^{-1} p_\alpha,
\]

(37)

where

\[
P_\alpha = P - p_\alpha.
\]

(38)

Physically this means that a particular polarization \( p_\alpha \) should not participate again in the screening process so that it should be subtracted out from \( P \). To distinguish it from self-screening, we have referred to this type of process as ”self-polarization” although in essence it is also a self-screening process.

Analogous to the self-screening correction described before, the self-polarization correction may be regarded as an approximate way of including the exchange diagrams. Consider the first order direct and exchange terms. The direct term is given by
\[ P_d(x_1, x_2) = - \int d^t x_1 d^t x_2 G(x_1, x_1) G(x_2, x_2) \times v(3 - 4) G(x, x_2) G(x_2, x_2). \] (39)

For the exchange term we have
\[ P_x(x_1, x_2) = \int d^t x_1 d^t x_2 G(x_1, x_1) G(x_2, x_2) \times G(x_3, x_2) G(x_1, x_3) v(3 - 4). \] (40)

Writing the Green functions in Fourier representation yields
\[ P_d(r_1, r_2; \omega) \]
\[ = - \int d^3 r_3 d^3 r_4 \int \frac{d\omega_1}{2\pi} G(r_3, r_1; \omega_1) G(r_1, r_3; \omega_1 + \omega) \]
\[ \times \int \frac{d\omega_3}{2\pi} G(r_4, r_2; \omega_3) G(r_4, r_2; \omega_3 + \omega) v(r_3 - r_4). \] (41)

and
\[ P_x(r_1, r_2; \omega) \]
\[ = \int d^3 r_3 d^3 r_4 \int \frac{d\omega_1}{2\pi} G(r_4, r_1; \omega_1) G(r_1, r_3; \omega_1 + \omega) \]
\[ \times \int \frac{d\omega_3}{2\pi} G(r_2, r_4; \omega_3) G(r_3, r_2; \omega_3 + \omega) v(r_3 - r_4). \] (42)

Using a non-interacting Green function of a given spin yields, using the convention that repeated indices are summed and \( n, n' \) refer to the occupied orbitals whereas \( m, m' \) to the unoccupied orbitals,
\[ P_d(r_1, r_2; \omega) = \frac{\phi_n^*(r_1) \phi_m(r_1) \epsilon_{nm, nm'} \phi_{n'}(r_2) \phi_{m'}^*(r_2)}{(\omega - \epsilon_m + \epsilon_n + i\delta)(\omega - \epsilon_{nm'} + \epsilon_{n'} + i\delta)} \]
\[ - \frac{\phi_n^*(r_1) \phi_{n'}(r_1) \epsilon_{nm, mm'} \phi_m(r_2) \phi_{m'}^*(r_2)}{(\omega - \epsilon_m + \epsilon_{n'} + i\delta)(\omega + \epsilon_{mm'} - \epsilon_{n} - i\delta)} \]
\[ + \frac{\phi_n^*(r_1) \phi_{m'}(r_1) \epsilon_{nm, nn'} \phi_{m'}(r_2) \phi_{m'}^*(r_2)}{(\omega + \epsilon_m - \epsilon_{n'} - i\delta)(\omega + \epsilon_{nn'} + \epsilon_m - i\delta)}. \] (43)

For the exchange term we obtain for a given spin
\[ P_x(r_1, r_2; \omega) = \frac{-\phi_n^*(r_1) \phi_{m'}(r_1) \epsilon_{mm, nn'} \phi_{m'}(r_2) \phi_{m'}^*(r_2)}{(\omega - \epsilon_m + \epsilon_n + i\delta)(\omega - \epsilon_{mm'} + \epsilon_{n} + i\delta)} \]
\[ + \frac{\phi_n^*(r_1) \phi_{m'}(r_1) \epsilon_{mm, mm'} \phi_{m'}(r_2) \phi_{m'}^*(r_2)}{(\omega + \epsilon_m - \epsilon_{n'} - i\delta)(\omega + \epsilon_{mm'} - \epsilon_{n'} + i\delta)} \]
\[ - \frac{\phi_n^*(r_1) \phi_{m'}(r_1) \epsilon_{mm, nn'} \phi_{m'}(r_2) \phi_{m'}^*(r_2)}{(\omega + \epsilon_m - \epsilon_{n'} - i\delta)(\omega + \epsilon_{nn'} - \epsilon_{n} - i\delta)}. \] (44)

where
\[ v_{ij,kl} = \int d^3 r d^3 r' \phi_i(r) \phi_j^*(r) v(r - r') \phi_k(r') \phi_l^*(r'). \] (45)

The two self-polarization terms, corresponding to \( n = n' \)
and \( m = m' \) in the second and third terms of \( P_x \), are cancelled by the corresponding terms in \( P_x \).

IV. APPLICATION TO A MODEL HYDROGEN DIMER

A. The HOMO-LUMO gap in the conventional GWA

Consider a model hydrogen molecule with one orbital centered on each atom. The two orbitals centered on different hydrogen atoms, \( \phi_1 \) and \( \phi_2 \), are normalized but not in general orthogonal: \( \langle \phi_1 | \phi_2 \rangle \neq 0 \). The one-particle eigenfunctions are the bonding and anti-bonding states:
\[ \psi_B = \frac{1}{\sqrt{2}} [\phi_1 + \phi_2], \] (46)
\[ \psi_A = \frac{1}{\sqrt{2}} [\phi_1 - \phi_2], \] (47)
with eigenenergies respectively \( \epsilon_B \) and \( \epsilon_A \). The indices \( A \) and \( B \) include the spin function \( \alpha \) and \( \beta \). These two eigenfunctions are orthonormal. We may assume that \( \phi_1 \) and \( \phi_2 \) are real. The two electrons occupy the bonding state with up and down spin. The non-interacting Green function (the up and down spin Green functions are identical) is given by
\[ G^0(r, r'; \omega) = \frac{\psi_B(r') \psi_B^*(r) + \psi_A(r') \psi_A^*(r)}{\omega - \epsilon_B - i\delta + \frac{\omega - \epsilon_A + i\delta}{2}}, \] (48)
where the one-particle Hamiltonian is taken to be the Hartree one. The HOMO-LUMO gap in the Hartree approximation is
\[ \Delta^H = \epsilon_A - \epsilon_B = 2t, \] (49)
where the hopping integral is given by
\[ t = -\left\langle \phi_1 | -\frac{1}{2} \nabla^2 + v_{\text{ext}} + V_H | \phi_2 \right\rangle. \] (50)

The onsite and intersite Coulomb interactions are respectively
\[ U_0 = \left\langle \phi_1^2 | v_{\phi_1^2} \right\rangle = \left\langle \phi_2^2 | v_{\phi_2^2} \right\rangle, \] (51)
\[ U_1 = \left\langle \phi_1^2 | v_{\phi_2^2} \right\rangle. \] (52)
The matrix elements in the bonding and anti-bonding states are

\[
\langle \psi_B | \Sigma^c | \psi_B \rangle = -v(r - r') \psi_B(r) \psi_B(r').
\]

The HOMO-LUMO gap in the HFA is therefore

\[
\Delta^{\text{HFA}} = 2t + U_1.
\]

We now proceed to calculate the correlation part of the self-energy. The polarization function can be written in the form

\[
P_0(r, r'; \omega) = \psi_B(r) \psi_A(r) P^0(\omega) \psi_B(r') \psi_A(r'),
\]

where

\[
P^0(\omega) = 2 \left\{ \frac{1}{\omega - \Delta \varepsilon + i\delta} - \frac{1}{\omega + \Delta \varepsilon - i\delta} \right\}
\]

with \( \Delta \varepsilon = \varepsilon_A - \varepsilon_B \).

The factor of 2 in (53) is due to the sum over spin. Using the RPA equation in (56) and solving it by iteration, it is straightforward to see that each term in the iterative solution can be written in the same form as \( P^0 \) so that the response function can also be written as

\[
R(r, r'; \omega) = \psi_B(r) \psi_A(r) R(\omega) \psi_B(r') \psi_A(r').
\]

\( R(\omega) \) can be calculated algebraically and it is given by

\[
R(\omega) = \frac{2r}{\omega - \Delta E + i\delta} - \frac{2r}{\omega + \Delta E - i\delta},
\]

where

\[
\Delta E = (\Delta \varepsilon)^2 + 4v_{B,A,B,A} \Delta \varepsilon.
\]

\[
v_{ab,cd} = \int d^3rd^3r' \psi_a(r) \psi_b(r) v(r - r') \psi_c(r') \psi_d(r'),
\]

\[
r = \frac{\Delta \varepsilon}{\Delta E} < 1,
\]

\[
= \frac{1}{\sqrt{1 + \frac{2(U_0 - U_1)}{\Delta \varepsilon}}}
\]

\[
\approx 1 - \frac{U_0 - U_1}{2t}.
\]

Using

\[
W^c(r', r; \omega) = \int d^3r_1 d^3r_2 v(r' - r_1) R(r_1, r_2; \omega) v(r_2 - r),
\]

the correlation part of the self-energy \( \Sigma^c \) can be calculated analytically to yield

\[
\Sigma^c_{\text{GW}}(r, r'; \omega) = i \int \frac{d\omega'}{2\pi} \Sigma^0(r, r'; \omega + \omega') W^c(r', r; \omega')
\]

\[
= \frac{\lambda_1(r, r')}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{\lambda_2(r, r')}{\omega - \Delta E - \varepsilon_A + i\delta},
\]

where

\[
\lambda_1(r, r') = 2r \psi_B(r) \psi_B(r') \int d^3r_1 d^3r_2 v(r - r_1) \times \psi_B(r_1) \psi_A(r_1) \psi_B(r_2) \psi_B(r_2) v(r_2 - r'),
\]

\[
\lambda_2(r, r') = 2r \psi_A(r) \psi_A(r') \int d^3r_1 d^3r_2 v(r - r_1) \times \psi_B(r_1) \psi_A(r_1) \psi_A(r_2) \psi_B(r_2) v(r_2 - r'),
\]

\[
\langle \psi_B | \Sigma^c_{\text{GW}}(\omega) | \psi_B \rangle = \frac{2r v_{BB,AB}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{2r v_{AB,AA}^2}{\omega - \Delta E - \varepsilon_A + i\delta}
\]

\[
= \frac{1}{2} \frac{r(U_0 - U_1)^2}{\omega - \Delta E + \varepsilon_B - i\delta}.
\]

Adding to the Hartree-Fock gap in (56) the HOMO-LUMO gap in the GWA is therefore

\[
\Delta^{GWA} = 2t + U_1 + \frac{r(U_0 - U_1)^2}{\Delta \varepsilon + \Delta E}.
\]

It is interesting to note that correlation effects increase the Hartree-Fock gap, counter to the usual expectation.
B. The HOMO-LUMO gap in the GWA with self-screening correction

Let us now apply our \( GW \) with self-screening correction scheme. For an electron of a given spin in the bonding or anti-bonding state the screening is provided by the other electron with opposite spin, as it should. Thus, the polarization is half of the polarization without self-screening correction. The calculation proceeds as in the previous section and we obtain

\[
R(\omega) = \frac{r}{\omega - \Delta E + i\delta} - \frac{r}{\omega + \Delta E - i\delta}, \quad (72)
\]

where

\[
\Delta E = \sqrt{(\Delta \varepsilon)^2 + 2\nu_{BA,BA} \Delta \varepsilon}, \quad r = \frac{\Delta \varepsilon}{\Delta E}. \quad (73)
\]

The correlation part of the self-energy with self-screening correction is

\[
\Sigma_{GW-SA}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{2} \frac{\lambda_1(\mathbf{r}, \mathbf{r}')}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{1}{2} \frac{\lambda_2(\mathbf{r}, \mathbf{r}')}{\omega - \Delta E - \varepsilon_A + i\delta}, \quad (74)
\]

where \( \lambda_1 \) and \( \lambda_2 \) are given in (67) and (68). Thus,

\[
\langle \psi_B | \Sigma_{GW-SA}(\omega) | \psi_B \rangle = \frac{2r v_{BB,BA}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{2r v_{AB,AB}^2}{\omega - \Delta E - \varepsilon_A + i\delta}, \quad (75)
\]

\[
\langle \psi_A | \Sigma_{GW-SA}(\omega) | \psi_A \rangle = \frac{2r v_{AB,BA}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{2r v_{AA,AB}^2}{\omega - \Delta E - \varepsilon_A + i\delta}, \quad (76)
\]

Taking into account the Hartree-Fock gap in (50), the self-screening-corrected \( GW \) HOMO-LUMO gap is therefore

\[
\Delta_{GW-SA} = 2t + U_1 + \frac{r(U_0 - U_1)^2}{2(\Delta \varepsilon + \Delta E)}, \quad (77)
\]

where

\[
r = \frac{\Delta \varepsilon}{\Delta E} = \left[ 1 + \frac{U_0 - U_1}{\Delta \varepsilon} \right]^{-1/2}. \quad (78)
\]

It is shown below that this is the same as the exact result up to second order in \((U_0 - U_1)/2t\) in the weak to moderate coupling regime where \((U_0 - U_1)/2t < 1\).

C. Exact solution in atomic basis

We consider configurations with total \( S_z = 0 \). In this case the Hamiltonian is given by

\[
H = \begin{pmatrix}
2\varepsilon_0 + U_1 & 0 & -t & -t \\
0 & 2\varepsilon_0 + U_1 & t & t \\
-t & t & 2\varepsilon_0 + U_0 & 0 \\
-t & t & 0 & 2\varepsilon_0 + U_0
\end{pmatrix},
\]

which can be solved analytically. Since \( \varepsilon_0 \) appears only in the diagonal element, we may set it to zero. Choosing \( \varepsilon_0 = 0 \), the ground-state energy is given by

\[
E_0(N) = \frac{1}{2}(U_0 + U_1) - \frac{1}{2} \sqrt{(U_0 - U_1)^2 + 16t^2}. \quad (80)
\]

To calculate the bonding-antibonding or HOMO-LUMO gap, we need to consider the \( N \pm 1 \) problems. For the one- and three-electron problem there are only two configurations. The eigenvalues are

\[
E_{1,2}(N + 1) = 3\varepsilon_0 + U_0 + 2U_1 \pm (-t), \quad (81)
\]

\[
E_{1,2}(N - 1) = \varepsilon_0 \pm t. \quad (82)
\]

The exact HOMO-LUMO gap with \( t > 0 \) is

\[
\Delta_{\text{exact}} = E_{1}(N + 1) - 2E_0(N) + E_{1}(N - 1) = -2t + U_1 + \sqrt{(U_0 - U_1)^2 + 16t^2}. \quad (83)
\]

It approaches \( 2t \) as \( U_{0,1} \to 0 \), as it should. In the weak or moderate coupling regime where \((U_0 - U_1)/2t < 1\) and the gap is given by

\[
\Delta_{\text{exact}} \approx 2t + U_1 + \frac{t}{2} \left( \frac{U_0 - U_1}{2t} \right)^2. \quad (84)
\]

This is the same as the gap in the \( GW \) scheme with self-screening correction up to order \((U_0 - U_1)/2t)^2:\n
\[
\Delta_{GW-SA} = 2t + U_1 + \frac{r(U_0 - U_1)^2}{2(\Delta \varepsilon + \Delta E)} \approx 2t + U_1 + \frac{t}{2} \left( \frac{U_0 - U_1}{2t} \right)^2. \quad (85)
\]

V. Conclusion

We have proposed a scheme for taking into account self-screening correction within the GWA. The scheme introduces orbital and spin dependent screened interaction. While this is not necessary in theory, the introduction of
orbital and spin dependence $W$ within the GWA captures the essential physics better and improves the self-energy without resorting to complicated vertex corrections. This is analogous to the introduction of the spin variable in the spin density functional theory. The scheme is justified theoretically by showing that the self-screening terms are indeed cancelled when exchange diagrams beyond the GWA are considered. When applied to a model hydrogen dimer, the scheme reproduces the exact result in the weak to moderate coupling regime. Work is now under way to apply the scheme to real systems.

VI. ACKNOWLEDGMENT

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