

***GW* approximation with self-screening correction**F. Aryasetiawan,<sup>1</sup> R. Sakuma,<sup>1</sup> and K. Karlsson<sup>2</sup><sup>1</sup>*Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba 263-8522, Japan*<sup>2</sup>*Department of Life Sciences, Högskolan i Skövde, SE-54128 Skövde, Sweden*

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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 is 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 that 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 on-site and off-site Hubbard interaction parameters and  $t$  is the hopping parameter.

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**I. INTRODUCTION**

In the Hartree approximation,<sup>1</sup> a system of electrons moves 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).<sup>2</sup> In density functional theory,<sup>3</sup> Perdew and Zunger introduced the concept of self-interaction correction<sup>4</sup> 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  $k = k_F$ .<sup>5</sup> 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).<sup>6,7</sup> 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 free from self-interaction. However, it is contaminated by “self-screening” in that an electron screens itself. This is 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 is thought to be a source of significant errors in the electronic structure. The self-screening problem can 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.<sup>8</sup> Evidently, since there is only one electron, upon removal of the electron there are no other electrons that can screen the remaining hole, so 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 long been suspected 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 found that the GWA overscreens the Hartree-Fock ionization potential, leading to an underestimation by 0.4–0.5 eV compared to experiment.<sup>9</sup> 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.<sup>10</sup> It is very likely that this error originates from self-screening. From a physical viewpoint, 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 scheme that 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).<sup>11</sup> 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 theoretical support for the scheme by showing from a diagrammatic viewpoint that the removal of the self-screening terms is partially equivalent to adding exchange diagrams. In other words, the self-screening terms are canceled 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, which allows 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 on-site and off-site 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 noninteracting Green function into its orbital components:

$$G_{\sigma}^0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n g_{n\sigma}(\mathbf{r}, \mathbf{r}'; \omega), \quad (1)$$

$$g_{n\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\varphi_{n\sigma}(\mathbf{r})\varphi_{n\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{n\sigma}}, \quad (2)$$

$$h\varphi_{n\sigma} = \varepsilon_{n\sigma}\varphi_{n\sigma}, \quad (3)$$

where  $h$  is a one-particle Hamiltonian,  $\varepsilon_{n\sigma} \rightarrow \varepsilon_{n\sigma} + i\delta$  for an occupied state, and  $\varepsilon_{n\sigma} \rightarrow \varepsilon_{n\sigma} - i\delta$  for an unoccupied state. We refer to  $\{g_{n\sigma}\}$  as orbital Green functions. In the GWA, the self-energy is given by, using a noninteracting  $G^0$ ,

$$\begin{aligned} \Sigma_{\sigma}(\mathbf{r}t, \mathbf{r}'t') &= iG_{\sigma}^0(\mathbf{r}t, \mathbf{r}'t')W(\mathbf{r}'t', \mathbf{r}t) \\ &= i\sum_m g_{m\sigma}(\mathbf{r}t, \mathbf{r}'t')W(\mathbf{r}'t', \mathbf{r}t), \end{aligned} \quad (4)$$

where  $W$  is the screened interaction,

$$W = \epsilon^{-1}v, \quad (5)$$

with  $\epsilon$  being the dielectric matrix.

Consider an electron occupying an orbital  $\varphi_{m\sigma}$  propagating from  $(\mathbf{r}'t')$  to  $(\mathbf{r}t)$  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. We therefore define the following Green function:

$$G_{m\sigma} = G_{\sigma} - g_{m\sigma}, \quad (6)$$

where  $G_{m\sigma}$  is now the Green function without  $g_{m\sigma}$ . We also introduce the polarization  $P_{m\sigma}$ , 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,

$$P_{m\sigma} = -i(G_{m\sigma}G_{m\sigma} + G_{-\sigma}G_{-\sigma}) \quad (7)$$

(a)  $\Sigma^{\text{GW}} = \frac{W}{g_1} + \frac{W}{g_2} \dots$

(b)  $\Sigma^{\text{GW-SS}} = \frac{W_1}{g_1} + \frac{W_2}{g_2} \dots$

FIG. 1. Comparison between the self-energy diagrams in the conventional GWA (a) and the GWA with self-screening correction (b). In the latter, the screened interaction depends on both the orbital and spin of the electron represented by  $g_n$ , as discussed in the text.

and the corresponding response function is given by

$$R_{m\sigma} = P_{m\sigma} + P_{m\sigma}vR_{m\sigma}. \quad (8)$$

With this response function, the screened interaction becomes

$$W_{m\sigma} = v + vR_{m\sigma}v = v + W_{m\sigma}^c. \quad (9)$$

The self-energy then takes the following form:

$$\Sigma_{\sigma}(\mathbf{r}t, \mathbf{r}'t') = i\sum_m g_{m\sigma}(\mathbf{r}t, \mathbf{r}'t')W_{m\sigma}(\mathbf{r}'t', \mathbf{r}t). \quad (10)$$

In Fig. 1, the self-energy diagrams corresponding to Eq. (10) are compared with the conventional  $GW$  diagrams.

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

$$\begin{aligned} \Sigma_{\sigma}^c(\mathbf{r}, \mathbf{r}'; \omega) &= i\sum_m \int \frac{d\omega'}{2\pi} g_{m\sigma}(\mathbf{r}, \mathbf{r}'; \omega + \omega')W_m^c(\mathbf{r}', \mathbf{r}; \omega') \\ &= i\sum_m \int \frac{d\omega'}{2\pi} \frac{\varphi_{m\sigma}(\mathbf{r})\varphi_{m\sigma}^*(\mathbf{r}')W_m^c(\mathbf{r}', \mathbf{r}; \omega')}{\omega + \omega' - \varepsilon_{m\sigma} + i\delta \text{sgn}(\varepsilon_{m\sigma} - \mu)}. \end{aligned} \quad (11)$$

Writing the correlation part of the screened interaction,  $W^c$ , in its spectral representation,

$$\begin{aligned} W_{m\sigma}^c(\mathbf{r}', \mathbf{r}; \omega') &= \int_{-\infty}^0 d\omega'' \frac{D_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega'')}{\omega' - \omega'' - i\delta} \\ &\quad + \int_0^{\infty} d\omega'' \frac{D_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega'')}{\omega' - \omega'' + i\delta}, \end{aligned} \quad (12)$$

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

$$\Sigma_{\sigma}^{\text{occ}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_m^{\text{occ}} \int_0^{\infty} d\omega'' \frac{\varphi_{m\sigma}(\mathbf{r})D_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega'')\varphi_{m\sigma}^*(\mathbf{r}')}{\omega + \omega'' - \varepsilon_{m\sigma} - i\delta}, \quad (13)$$

$$\Sigma_{\sigma}^{\text{unocc}}(\mathbf{r}, \mathbf{r}'; \omega) = \sum_m^{\text{unocc}} \int_0^{\infty} d\omega'' \frac{\varphi_{m\sigma}(\mathbf{r})D_{m\sigma}(\mathbf{r}', \mathbf{r}; \omega'')\varphi_{m\sigma}^*(\mathbf{r}')}{\omega - \omega'' - \varepsilon_{m\sigma} + i\delta}. \quad (14)$$

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

$$D_{m\sigma}(-\omega) = -D_{m\sigma}(\omega), \quad W_{m\sigma}^c(-\omega) = W_{m\sigma}^c(\omega), \quad (15)$$

and

$$D_{m\sigma}(\omega) = -\frac{1}{\pi} \text{Im} W_{m\sigma}^c(\omega) \text{sgn}(\omega). \quad (16)$$

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 Eq. (10). Each electron experiences a different screened interaction  $W_{m\sigma}$  that 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 a 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 true system and captures the essential physics so that a relatively simple approximation, such as the local spin density approximation, still works well. A presumably much more complicated functional would be required to achieve the same level of accuracy for the total energy if the total density were to be used instead. A similar situation arises in our case, in which the orbital- and spin-dependent screened interactions closely mirror the physical situation and thereby promote 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.

It is interesting to ask if the scheme can be made self-consistent. Full self-consistency in the sense of having a renormalized Green function is beyond the present scheme because it relies on the expansion of the self-energy in terms of a noninteracting Green function, which is diagonal in the one-particle eigenfunctions and can therefore be decomposed into

its orbital components as in Eq. (1), whereas a renormalized Green function is generally not diagonal. However, partial self-consistency can be achieved by updating the one-particle wave functions and eigenvalues in Eq. (2), and several techniques are available for performing this updating within the so-called quasiparticle self-consistency scheme.<sup>12-14</sup> The self-energy obtained from a starting  $G^0$  is used to construct a new set of one-particle or quasiparticle wave functions and eigenvalues, which in turn are used to construct a new  $G^0$ . The cycle is continued until self-consistency in the one-particle spectrum is achieved. In this way, the self-screening scheme proposed in this paper becomes independent of the starting  $G^0$ . Such self-consistency may be important in systems in which the starting  $G^0$ , which is usually constructed from the LDA wave functions and eigenvalues, deviates significantly from the true quasiparticle wave functions and energies.

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

The self-screening correction tends to vanish for each individual extended state. However, when summation is performed over continuous quantum labels as in Eq. (10), the self-screening correction may be finite. Indeed, from a physical point of view, we expect that the self-screening correction is significant when the extended state originates from a localized orbital such as a  $3d$  or a  $4f$  orbital. Performing the sum in Eq. (10) for extended states, however, can be numerically very challenging so that in practice an approximate scheme is necessary. Below, we present an approximate scheme based on the expansion of the states in maximally localized Wannier orbitals.

Consider expanding a given Bloch state  $\psi_{\mathbf{k}\sigma}$  in its Wannier representation,<sup>15</sup>

$$\psi_{\mathbf{k}\sigma}(\mathbf{r}) = \sum_m U_{nm}(\mathbf{k}) \psi_{\mathbf{k}m\sigma}^w(\mathbf{r}), \quad (17)$$

$$\psi_{\mathbf{k}m\sigma}^w(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) \chi_{\mathbf{R}m\sigma}(\mathbf{r}), \quad (18)$$

where  $U$  is chosen to maximally localize the Wannier orbitals  $\{\chi_{\mathbf{R}m\sigma}\}$ . We assume for simplicity that  $U$  is a unitary matrix, which is not necessarily the case for entangled bands. The Green function is, with  $\varepsilon_{\mathbf{k}\sigma} \rightarrow \varepsilon_{\mathbf{k}\sigma} + i\eta$  for occupied states and  $\varepsilon_{\mathbf{k}\sigma} \rightarrow \varepsilon_{\mathbf{k}\sigma} - i\eta$  for unoccupied states,

$$\begin{aligned} G_{\sigma}^0(\mathbf{r}, \mathbf{r}'; \omega) &= \sum_{kn} \frac{\psi_{\mathbf{k}\sigma}(\mathbf{r}) \psi_{\mathbf{k}\sigma}^*(\mathbf{r}')}{\omega - \varepsilon_{\mathbf{k}\sigma}} \\ &= \frac{1}{N} \sum_{\mathbf{k}n} \sum_{mm'} \sum_{\mathbf{R}\mathbf{R}'} \exp[i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \frac{U_{nm}(\mathbf{k}) \chi_{\mathbf{R}m\sigma}(\mathbf{r}) \chi_{\mathbf{R}'m'\sigma}^*(\mathbf{r}') U_{m'n}^{\dagger}(\mathbf{k})}{\omega - \varepsilon_{\mathbf{k}\sigma}} \\ &= \frac{1}{N} \sum_{\mathbf{k}n} \sum_{mm'} \sum_{\mathbf{R} \neq \mathbf{R}'} \exp[i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')] \frac{U_{nm}(\mathbf{k}) \chi_{\mathbf{R}m\sigma}(\mathbf{r}) \chi_{\mathbf{R}'m'\sigma}^*(\mathbf{r}') U_{m'n}^{\dagger}(\mathbf{k})}{\omega - \varepsilon_{\mathbf{k}\sigma}} \\ &\quad + \frac{1}{N} \sum_{\mathbf{k}n} \sum_{mm'} \sum_{\mathbf{R}} \frac{U_{nm}(\mathbf{k}) \chi_{\mathbf{R}m\sigma}(\mathbf{r}) \chi_{\mathbf{R}m'\sigma}^*(\mathbf{r}') U_{m'n}^{\dagger}(\mathbf{k})}{\omega - \varepsilon_{\mathbf{k}\sigma}}. \end{aligned} \quad (19)$$

We apply the self-screening correction to the component of  $G_\sigma^0$  corresponding to  $\mathbf{R} = \mathbf{R}'$ . As before, we define

$$G_{n\sigma}^0 = G_\sigma^0 - g_{n\sigma}, \quad (20)$$

$$g_{n\sigma}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{N} \sum_{\mathbf{k}} \sum_{mm'} \sum_{\mathbf{R}} \frac{U_{nm}(\mathbf{k}) \chi_{\mathbf{R}m\sigma}(\mathbf{r}) \chi_{\mathbf{R}m'\sigma}^*(\mathbf{r}') U_{m'n}^\dagger(\mathbf{k})}{\omega - \varepsilon_{\mathbf{k}n\sigma}}. \quad (21)$$

For a very narrow band such as the one formed by semicore states, we may make the following approximation:

$$g_{n\sigma}(\mathbf{r}, \mathbf{r}'; \omega) \approx \frac{1}{N} \sum_{\mathbf{R}} \frac{\chi_{\mathbf{R}n\sigma}(\mathbf{r}) \chi_{\mathbf{R}n\sigma}^*(\mathbf{r}')}{\omega - \langle \varepsilon_{n\sigma} \rangle}, \quad (22)$$

$$\langle \varepsilon_{n\sigma} \rangle = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}n\sigma}, \quad (23)$$

where we have used the unitarity of  $U$ . For a given site  $R$ , the orbital Green function  $g_{n\sigma}$  is confined to the site and it is equivalent to a core state Green function.

The above approximation, however, suffers from arbitrariness in the choice of the orbitals. The situation is similar to, for example, the LDA + U scheme,<sup>16</sup> in which an arbitrary choice of localized orbitals has to be made. Considering that the self-screening scheme itself is semiphenomenological, the arbitrariness in the choice of localized orbitals is a reasonable compromise for the large numerical simplification associated with the approximation.

### 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 canceled 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,<sup>17</sup> the second-order exchange self-energy for a given spin is

$$\Sigma^x(x_1, x_2) = (i)^2 \int dx_3 dx_4 G(x_1, x_3) G(x_3, x_4) \times G(x_4, x_2) v(x_1 - x_4) v(x_3 - x_2), \quad (24)$$

where  $x = (\mathbf{r}, t)$  and

$$v(x - x') = v(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (25)$$

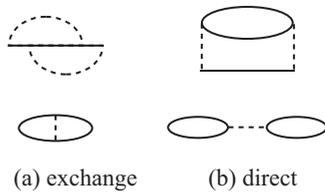


FIG. 2. The second-order exchange and direct self-energy and polarization diagrams. As shown in the text, the exchange diagrams cancel the self-screening terms in the direct diagrams.

Fourier transformation with respect to  $\tau = t_1 - t_2$  yields

$$\Sigma^x(\mathbf{r}_1, \mathbf{r}_2; \omega) = - \int d^3 r_3 d^3 r_4 \int \frac{d\omega_1 d\omega_2}{(2\pi)^2} G(\mathbf{r}_1, \mathbf{r}_3; \omega_1) \times G(\mathbf{r}_3, \mathbf{r}_4; \omega_2) G(\mathbf{r}_4, \mathbf{r}_2; \omega - \omega_1 + \omega_2) \times v(\mathbf{r}_1 - \mathbf{r}_4) v(\mathbf{r}_3 - \mathbf{r}_2). \quad (26)$$

Using a noninteracting Green function of a given spin

$$G^0(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\varphi_n(\mathbf{r}) \varphi_n^*(\mathbf{r}')}{\omega - \varepsilon_n - i\delta} + \sum_m \frac{\varphi_m(\mathbf{r}) \varphi_m^*(\mathbf{r}')}{\omega - \varepsilon_m + i\delta}, \quad (27)$$

we can perform the frequency integral over  $\omega_2$  using Cauchy's theorem by closing the contour either in the upper or lower plane:

$$\int \frac{d\omega_2}{2\pi} G^0(\mathbf{r}_3, \mathbf{r}_4; \omega_2) G^0(\mathbf{r}_4, \mathbf{r}_2; \omega - \omega_1 + \omega_2) = i \sum_n^{\text{occ}} \sum_m^{\text{unocc}} \left\{ \frac{\varphi_n(\mathbf{r}_3) \varphi_n^*(\mathbf{r}_4) \varphi_m(\mathbf{r}_4) \varphi_m^*(\mathbf{r}_2)}{\omega - \omega_1 + \varepsilon_n - \varepsilon_m + i\delta} + \frac{\varphi_m(\mathbf{r}_3) \varphi_m^*(\mathbf{r}_4) \varphi_n(\mathbf{r}_4) \varphi_n^*(\mathbf{r}_2)}{\omega - \omega_1 + \varepsilon_m - \varepsilon_n - i\delta} \right\}. \quad (28)$$

Similarly, integrating over  $\omega_1$ , we find

$$\Sigma^x(\mathbf{r}_1, \mathbf{r}_2; \omega) = - \sum_n^{\text{occ}} \sum_m^{\text{unocc}} \int d^3 r_3 d^3 r_4 v(\mathbf{r}_1 - \mathbf{r}_4) v(\mathbf{r}_3 - \mathbf{r}_2) \times \left\{ \sum_k^{\text{occ}} \frac{\varphi_k(\mathbf{r}_1) \varphi_k^*(\mathbf{r}_3) \varphi_m(\mathbf{r}_3) \varphi_m^*(\mathbf{r}_4) \varphi_n(\mathbf{r}_4) \varphi_n^*(\mathbf{r}_2)}{\omega - \varepsilon_k + \varepsilon_m - \varepsilon_n - i\delta} + \sum_k^{\text{unocc}} \frac{\varphi_k(\mathbf{r}_1) \varphi_k^*(\mathbf{r}_3) \varphi_n(\mathbf{r}_3) \varphi_n^*(\mathbf{r}_4) \varphi_m(\mathbf{r}_4) \varphi_m^*(\mathbf{r}_2)}{\omega - \varepsilon_k + \varepsilon_n - \varepsilon_m + i\delta} \right\}. \quad (29)$$

The second-order direct self-energy is

$$\Sigma^d(x_1, x_2) = -(i)^2 \int dx_3 dx_4 G(x_1, x_2) G(x_3, x_4) G(x_4, x_3) \times v(x_1 - x_4) v(x_3 - x_2), \quad (30)$$

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

$$\Sigma^d(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int d^3 r_3 d^3 r_4 \int \frac{d\omega_1 d\omega_2}{(2\pi)^2} G(\mathbf{r}_1, \mathbf{r}_2; \omega_1) \times G(\mathbf{r}_3, \mathbf{r}_4; \omega_2) G(\mathbf{r}_4, \mathbf{r}_3; \omega - \omega_1 + \omega_2) \times v(\mathbf{r}_1 - \mathbf{r}_4) v(\mathbf{r}_3 - \mathbf{r}_2), \quad (31)$$

which can be calculated analytically as in the exchange case yielding

$$\Sigma^d(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_n^{\text{occ}} \sum_m^{\text{unocc}} \int d^3 r_3 d^3 r_4 v(\mathbf{r}_1 - \mathbf{r}_4) v(\mathbf{r}_3 - \mathbf{r}_2) \times \left\{ \sum_k^{\text{occ}} \frac{\varphi_k(\mathbf{r}_1) \varphi_k^*(\mathbf{r}_2) \varphi_m(\mathbf{r}_3) \varphi_m^*(\mathbf{r}_4) \varphi_n(\mathbf{r}_4) \varphi_n^*(\mathbf{r}_3)}{\omega - \varepsilon_k + \varepsilon_m - \varepsilon_n - i\delta} + \sum_k^{\text{unocc}} \frac{\varphi_k(\mathbf{r}_1) \varphi_k^*(\mathbf{r}_2) \varphi_n(\mathbf{r}_3) \varphi_n^*(\mathbf{r}_4) \varphi_m(\mathbf{r}_4) \varphi_m^*(\mathbf{r}_3)}{\omega - \varepsilon_k + \varepsilon_n - \varepsilon_m + i\delta} \right\}. \quad (32)$$

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

$$\frac{\varphi_k(\mathbf{r}_1)\varphi_k^*(\mathbf{r}_2)\varphi_m(\mathbf{r}_3)\varphi_m^*(\mathbf{r}_4)\varphi_k(\mathbf{r}_4)\varphi_k^*(\mathbf{r}_3)}{\omega - \varepsilon_k + \varepsilon_m - \varepsilon_k - i\delta}, \quad (33)$$

where  $\varphi_m$  is unoccupied, are canceled by the corresponding terms in  $\Sigma^x$ . This is similar to the case in which  $\varphi_k$  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 developed a scheme for removing the self-screening in the random-phase approximation (RPA)<sup>11</sup> 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 in which 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

$$\begin{aligned} P(\mathbf{r}, \mathbf{r}'; \omega) &= \sum_{\alpha} \left\{ \frac{d_{\alpha}(\mathbf{r})d_{\alpha}^*(\mathbf{r}')}{\omega - \Delta_{\alpha}} - \frac{d_{\alpha}(\mathbf{r}')d_{\alpha}^*(\mathbf{r})}{\omega + \Delta_{\alpha}} \right\} \\ &= \sum_{\alpha} p_{\alpha}(\mathbf{r}, \mathbf{r}'; \omega), \end{aligned} \quad (34)$$

$$d_{\alpha}(\mathbf{r}) = \varphi_m(\mathbf{r})\varphi_n^*(\mathbf{r}), \quad (35)$$

$$\Delta_{\alpha} = \varepsilon_m - \varepsilon_n - i\delta, \quad \varepsilon_m > \mu, \quad \varepsilon_n \leq \mu.$$

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

$$\begin{aligned} R &= [1 - Pv]^{-1}P \\ &= P + PvP + PvPvP + \dots \end{aligned} \quad (36)$$

We can think of  $[1 - Pv]^{-1} = \epsilon^{-1}$  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:

$$R = \sum_{\alpha} [1 - P_{\alpha}v]^{-1}p_{\alpha}, \quad (37)$$

where

$$P_{\alpha} = P - p_{\alpha}. \quad (38)$$

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

$$\begin{aligned} P_d(x_1, x_2) &= - \int dx_3 dx_4 G(x_3, x_1)G(x_1, x_3) \\ &\quad \times v(x_3 - x_4)G(x_4, x_2)G(x_2, x_4). \end{aligned} \quad (39)$$

For the exchange term, we have

$$\begin{aligned} P_x(x_1, x_2) &= \int dx_3 dx_4 G(x_4, x_1)G(x_2, x_4) \\ &\quad \times G(x_3, x_2)G(x_1, x_3)v(x_3 - x_4). \end{aligned} \quad (40)$$

Writing the Green functions in Fourier representation yields

$$\begin{aligned} P_d(\mathbf{r}_1, \mathbf{r}_2; \omega) &= - \int d^3r_3 d^3r_4 \int \frac{d\omega_1}{2\pi} G(\mathbf{r}_3, \mathbf{r}_1; \omega_1)G(\mathbf{r}_1, \mathbf{r}_3; \omega_1 + \omega) \\ &\quad \times \int \frac{d\omega_3}{2\pi} G(\mathbf{r}_2, \mathbf{r}_4; \omega_3)G(\mathbf{r}_4, \mathbf{r}_2; \omega_3 + \omega)v(\mathbf{r}_3 - \mathbf{r}_4) \end{aligned} \quad (41)$$

and

$$\begin{aligned} P_x(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \int d^3r_3 d^3r_4 \int \frac{d\omega_1}{2\pi} G(\mathbf{r}_4, \mathbf{r}_1; \omega_1)G(\mathbf{r}_1, \mathbf{r}_3; \omega_1 + \omega) \\ &\quad \times \int \frac{d\omega_3}{2\pi} G(\mathbf{r}_2, \mathbf{r}_4; \omega_3)G(\mathbf{r}_3, \mathbf{r}_2; \omega_3 + \omega)v(\mathbf{r}_3 - \mathbf{r}_4). \end{aligned} \quad (42)$$

Using a noninteracting Green function of a given spin yields the following, using the convention that repeated indices are summed and  $n, n'$  refer to the occupied orbitals whereas  $m, m'$  to the unoccupied orbitals:

$$\begin{aligned} P_d(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \frac{\varphi_n^*(\mathbf{r}_1)\varphi_m(\mathbf{r}_1)v_{nm, n'm'}\varphi_{n'}(\mathbf{r}_2)\varphi_{m'}^*(\mathbf{r}_2)}{(\omega - \varepsilon_m + \varepsilon_n + i\delta)(\omega - \varepsilon_{m'} + \varepsilon_{n'} + i\delta)} \\ &\quad - \frac{\varphi_n^*(\mathbf{r}_1)\varphi_m(\mathbf{r}_1)v_{nm, m'n'}\varphi_{m'}(\mathbf{r}_2)\varphi_n^*(\mathbf{r}_2)}{(\omega - \varepsilon_m + \varepsilon_n + i\delta)(\omega + \varepsilon_{m'} - \varepsilon_{n'} - i\delta)} \\ &\quad - \frac{\varphi_m^*(\mathbf{r}_1)\varphi_n(\mathbf{r}_1)v_{mn, n'm'}\varphi_{n'}(\mathbf{r}_2)\varphi_{m'}^*(\mathbf{r}_2)}{(\omega + \varepsilon_m - \varepsilon_n - i\delta)(\omega - \varepsilon_{m'} + \varepsilon_{n'} + i\delta)} \\ &\quad + \frac{\varphi_m^*(\mathbf{r}_1)\varphi_n(\mathbf{r}_1)v_{mn, m'n'}\varphi_{m'}(\mathbf{r}_2)\varphi_n^*(\mathbf{r}_2)}{(\omega + \varepsilon_m - \varepsilon_n - i\delta)(\omega + \varepsilon_{m'} - \varepsilon_{n'} - i\delta)}. \end{aligned} \quad (43)$$

For the exchange term, we obtain for a given spin

$$\begin{aligned} P_x(\mathbf{r}_1, \mathbf{r}_2; \omega) &= - \frac{\varphi_n^*(\mathbf{r}_1)\varphi_m(\mathbf{r}_1)v_{nn', mm'}\varphi_{n'}(\mathbf{r}_2)\varphi_{m'}^*(\mathbf{r}_2)}{(\omega - \varepsilon_m + \varepsilon_n + i\delta)(\omega - \varepsilon_{m'} + \varepsilon_{n'} + i\delta)} \\ &\quad + \frac{\varphi_n^*(\mathbf{r}_1)\varphi_m(\mathbf{r}_1)v_{nm', mn'}\varphi_{m'}(\mathbf{r}_2)\varphi_n^*(\mathbf{r}_2)}{(\omega - \varepsilon_m + \varepsilon_n + i\delta)(\omega + \varepsilon_{m'} - \varepsilon_{n'} - i\delta)} \\ &\quad + \frac{\varphi_m^*(\mathbf{r}_1)\varphi_n(\mathbf{r}_1)v_{mn', nm'}\varphi_{n'}(\mathbf{r}_2)\varphi_{m'}^*(\mathbf{r}_2)}{(\omega + \varepsilon_m - \varepsilon_n - i\delta)(\omega - \varepsilon_{m'} + \varepsilon_{n'} + i\delta)} \\ &\quad - \frac{\varphi_m^*(\mathbf{r}_1)\varphi_n(\mathbf{r}_1)v_{mm', nn'}\varphi_{n'}(\mathbf{r}_2)\varphi_m^*(\mathbf{r}_2)}{(\omega + \varepsilon_m - \varepsilon_n - i\delta)(\omega + \varepsilon_{m'} - \varepsilon_{n'} - i\delta)}, \end{aligned} \quad (44)$$

where

$$v_{ij,kl} = \int d^3r d^3r' \varphi_i(\mathbf{r})\varphi_j^*(\mathbf{r}')v(\mathbf{r} - \mathbf{r}')\varphi_k^*(\mathbf{r}')\varphi_l(\mathbf{r}). \quad (45)$$

The two self-polarization terms, corresponding to  $n = n'$  and  $m = m'$  in the second and third terms of Eq. (43), are canceled 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,  $\varphi_1$  and  $\varphi_2$ , are normalized but not generally orthogonal:  $\langle \varphi_1 | \varphi_2 \rangle \neq 0$ . The one-particle eigenfunctions are the bonding and antibonding states:

$$\psi_B = \frac{1}{\sqrt{2}}[\varphi_1 + \varphi_2], \quad (46)$$

$$\psi_A = \frac{1}{\sqrt{2}}[\varphi_1 - \varphi_2], \quad (47)$$

with eigenenergies  $\varepsilon_B$  and  $\varepsilon_A$ , respectively. The indices  $A$  and  $B$  include the spin functions  $\alpha$  and  $\beta$ . These two eigenfunctions are orthonormal. We may assume that  $\varphi_1$  and  $\varphi_2$  are real. The two electrons occupy the bonding state with up and down spin. The noninteracting Green function (the up- and down-spin Green functions are identical) is given by

$$G^0(\mathbf{r}, \mathbf{r}'; \omega) = \frac{\psi_B(\mathbf{r})\psi_B(\mathbf{r}')}{\omega - \varepsilon_B - i\delta} + \frac{\psi_A(\mathbf{r})\psi_A(\mathbf{r}')}{\omega - \varepsilon_A + i\delta}, \quad (48)$$

where the one-particle Hamiltonian is taken to be the Hartree one. The HOMO-LUMO gap in the Hartree approximation is

$$\Delta^H = \varepsilon_A - \varepsilon_B = 2t, \quad (49)$$

where the hopping integral is given by

$$t = -\langle \varphi_1 | -\frac{1}{2}\nabla^2 + v_{\text{ext}} + V_H | \varphi_2 \rangle. \quad (50)$$

The on-site and intersite Coulomb interactions are, respectively,

$$U_0 = \langle \varphi_1^2 | v | \varphi_1^2 \rangle = \langle \varphi_2^2 | v | \varphi_2^2 \rangle, \quad (51)$$

$$U_1 = \langle \varphi_1^2 | v | \varphi_2^2 \rangle. \quad (52)$$

$\langle \varphi_1 \varphi_2 | v | \varphi_1 \varphi_2 \rangle$  and  $\langle \varphi_1^2 | v | \varphi_1 \varphi_2 \rangle$  are neglected since they are much smaller compared with  $U_0$  and  $U_1$ .

First, let us calculate the exchange contribution:

$$\Sigma^x(\mathbf{r}, \mathbf{r}') = -v(\mathbf{r} - \mathbf{r}')\psi_B(\mathbf{r})\psi_B(\mathbf{r}'). \quad (53)$$

The matrix elements in the bonding and antibonding states are

$$\langle \psi_B | \Sigma^x | \psi_B \rangle = -\frac{1}{2}(U_0 + U_1), \quad (54)$$

$$\langle \psi_A | \Sigma^x | \psi_A \rangle = -\frac{1}{2}(U_0 - U_1). \quad (55)$$

The HOMO-LUMO gap in the HFA is, therefore,

$$\Delta^{\text{HF}} = 2t + U_1. \quad (56)$$

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

$$P^0(\mathbf{r}, \mathbf{r}'; \omega) = \psi_B(\mathbf{r})\psi_A(\mathbf{r}')P^0(\omega)\psi_B(\mathbf{r}')\psi_A(\mathbf{r}), \quad (57)$$

where

$$P^0(\omega) = 2 \left\{ \frac{1}{\omega - \Delta\varepsilon + i\delta} - \frac{1}{\omega + \Delta\varepsilon - i\delta} \right\} \quad (58)$$

with

$$\Delta\varepsilon = \varepsilon_A - \varepsilon_B. \quad (59)$$

The factor of 2 in Eq. (58) is due to the sum over spin. Using the RPA equation in Eq. (36) 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

$$R(\mathbf{r}, \mathbf{r}'; \omega) = \psi_B(\mathbf{r})\psi_A(\mathbf{r}')R(\omega)\psi_B(\mathbf{r}')\psi_A(\mathbf{r}). \quad (60)$$

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

$$R(\omega) = \frac{2r}{\omega - \Delta E + i\delta} - \frac{2r}{\omega + \Delta E - i\delta}, \quad (61)$$

where

$$\Delta E = \sqrt{(\Delta\varepsilon)^2 + 4v_{BA,BA}\Delta\varepsilon}, \quad (62)$$

$$v_{ab,cd} = \int d^3r d^3r' \psi_a(\mathbf{r})\psi_b(\mathbf{r}')v(\mathbf{r} - \mathbf{r}')\psi_c(\mathbf{r}')\psi_d(\mathbf{r}), \quad (63)$$

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

$$= \frac{1}{\sqrt{1 + \frac{2(U_0 - U_1)}{\Delta\varepsilon}}} \approx 1 - \frac{U_0 - U_1}{2t}. \quad (64)$$

Using

$$W^c(\mathbf{r}', \mathbf{r}; \omega) = \int d^3r_1 d^3r_2 v(\mathbf{r}' - \mathbf{r}_1)R(\mathbf{r}_1, \mathbf{r}_2; \omega)v(\mathbf{r}_2 - \mathbf{r}), \quad (65)$$

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

$$\begin{aligned} \Sigma_{GW}^c(\mathbf{r}, \mathbf{r}'; \omega) &= i \int \frac{d\omega'}{2\pi} G^0(\mathbf{r}, \mathbf{r}'; \omega + \omega') W^c(\mathbf{r}', \mathbf{r}; \omega') \\ &= \frac{\lambda_1(\mathbf{r}, \mathbf{r}')}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{\lambda_2(\mathbf{r}, \mathbf{r}')}{\omega - \Delta E - \varepsilon_A + i\delta}, \end{aligned} \quad (66)$$

where

$$\begin{aligned} \lambda_1(\mathbf{r}, \mathbf{r}') &= 2r\psi_B(\mathbf{r})\psi_B(\mathbf{r}') \int d^3r_1 d^3r_2 v(\mathbf{r} - \mathbf{r}_1) \\ &\quad \times \psi_B(\mathbf{r}_1)\psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_2)v(\mathbf{r}_2 - \mathbf{r}'), \end{aligned} \quad (67)$$

$$\begin{aligned} \lambda_2(\mathbf{r}, \mathbf{r}') &= 2r\psi_A(\mathbf{r})\psi_A(\mathbf{r}') \int d^3r_1 d^3r_2 v(\mathbf{r} - \mathbf{r}_1) \\ &\quad \times \psi_B(\mathbf{r}_1)\psi_A(\mathbf{r}_1)\psi_A(\mathbf{r}_2)\psi_B(\mathbf{r}_2)v(\mathbf{r}_2 - \mathbf{r}'), \end{aligned} \quad (68)$$

$$\begin{aligned} \langle \psi_B | \Sigma_{GW}^c(\omega) | \psi_B \rangle &= \frac{2rv_{BB,AB}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{2rv_{AB,AB}^2}{\omega - \Delta E - \varepsilon_A + i\delta} \\ &= \frac{1}{2} \frac{r(U_0 - U_1)^2}{\omega - \Delta E - \varepsilon_A + i\delta}, \end{aligned} \quad (69)$$

$$\begin{aligned}
 & \langle \psi_A | \Sigma_{GW}^c(\omega) | \psi_A \rangle \\
 &= \frac{2rv_{AB,AB}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{2rv_{AA,AB}^2}{\omega - \Delta E - \varepsilon_A + i\delta} \\
 &= \frac{1}{2} \frac{r(U_0 - U_1)^2}{\omega + \Delta E - \varepsilon_B - i\delta}. \quad (70)
 \end{aligned}$$

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

$$\Delta^{GW} = 2t + U_1 + \frac{r(U_0 - U_1)^2}{\Delta\varepsilon + \Delta E}. \quad (71)$$

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 antibonding state, the screening is provided by the other electron with opposite spin, as it should be. 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

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

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

$$\begin{aligned}
 & \Sigma_{GW-SS}^c(\mathbf{r}, \mathbf{r}'; \omega) \\
 &= \frac{1}{2} \frac{\lambda_1(\mathbf{r}, \mathbf{r}')}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{1}{2} \frac{\lambda_2(\mathbf{r}, \mathbf{r}')}{\omega - \Delta E - \varepsilon_A + i\delta}, \quad (74)
 \end{aligned}$$

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

$$\begin{aligned}
 & \langle \psi_B | \Sigma_{GW-SS}^c(\omega) | \psi_B \rangle \\
 &= \frac{rv_{BB,AB}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{rv_{AB,AB}^2}{\omega - \Delta E - \varepsilon_A + i\delta} \\
 &= \frac{1}{4} \frac{r(U_0 - U_1)^2}{\omega - \Delta E - \varepsilon_A + i\delta}, \quad (75)
 \end{aligned}$$

$$\begin{aligned}
 & \langle \psi_A | \Sigma_{GW-SS}^c(\omega) | \psi_A \rangle \\
 &= \frac{rv_{AB,AB}^2}{\omega + \Delta E - \varepsilon_B - i\delta} + \frac{rv_{AA,AB}^2}{\omega - \Delta E - \varepsilon_A + i\delta} \\
 &= \frac{1}{4} \frac{r(U_0 - U_1)^2}{\omega + \Delta E - \varepsilon_B - i\delta}. \quad (76)
 \end{aligned}$$

Taking into account the Hartree-Fock gap in Eq. (56), the self-screening-corrected *GW* HOMO-LUMO gap is,

therefore,

$$\Delta^{GW-SS} = 2t + U_1 + \frac{r(U_0 - U_1)^2}{2(\Delta\varepsilon + \Delta E)}, \quad (77)$$

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 an atomic basis

We consider configurations with total  $S_z = 0$ . In this case, the Hamiltonian is given by

$$H = \begin{pmatrix} 2\varepsilon_0 + U_1 & 0 & -t & -t \\ 0 & 2\varepsilon_0 + U_1 & t & t \\ -t & t & 2\varepsilon_0 + U_0 & 0 \\ -t & t & 0 & 2\varepsilon_0 + U_0 \end{pmatrix}, \quad (79)$$

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

$$\begin{aligned}
 \Delta^{\text{exact}} &= E_1(N+1) - 2E_0(N) + E_1(N-1) \\
 &= -2t + U_1 + \sqrt{(U_0 - U_1)^2 + 16t^2}. \quad (83)
 \end{aligned}$$

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

$$\begin{aligned}
 \Delta^{\text{exact}} &= -2t + U_1 + \sqrt{(U_0 - U_1)^2 + 16t^2} \\
 &\approx 2t + U_1 + \frac{t}{2} \left( \frac{U_0 - U_1}{2t} \right)^2. \quad (84)
 \end{aligned}$$

This is the same as the gap in the *GW* scheme with self-screening correction up to order  $[(U_0 - U_1)/2t]^2$ :

$$\begin{aligned}
 \Delta^{GW-SS} &= 2t + U_1 + \frac{r(U_0 - U_1)^2}{2(\Delta\varepsilon + \Delta E)} \\
 &\approx 2t + U_1 + \frac{t}{2} \left( \frac{U_0 - U_1}{2t} \right)^2. \quad (85)
 \end{aligned}$$

### 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 canceled 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 underway to apply the scheme to real systems.

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