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Self-energy calculation of the hydrogen atom: Importance of the unbound states

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We present the calculation of the self-energy of the isolated hydrogen atom within the GW approximation starting from the noninteracting Green's function constructed from the exact wave functions of the hydrogen atom. The error in the electron removal energy of the $1s$ state is found to be about 0.02 eV, which is much smaller than what one would expect. This small error is explained by the cancellation of the self-screening errors between different l contributions of the self-energy. The unbound continuum states are found to be crucial to get the correct self-energy.

I. INTRODUCTION

After the pioneering work by Hybertsen and Louie [1,2] and Godby *et al.* [3], Hedin's GW approximation [4–6] has been widely used with great success in calculating the excited states of many semiconductors and molecules. Most of the calculations that have been performed so far are within the so-called G_0W_0 approximation approach starting from a noninteracting Hamiltonian, in most cases, the Kohn-Sham Hamiltonian within the local-density approximation (LDA) of density-functional theory [7]. The screened Coulomb interaction is calculated from the polarization function, which, within the G_0W_0 approach, has the same form as that of the random-phase approximation (RPA).

Despite its success, the G_0W_0 approach is found to be insufficient to treat localized states, such as the d bands of transition metals [8] or the semicore states of semiconductors [9]. One possible reason for this failure could be that, in the G_0W_0 approximation or RPA, the polarization function contains the unphysical self-screening effect where an electron shields the field produced by itself [10]. In order to improve the theory, careful analysis is required to identify the shortcomings of the GW approximation, but because of the complexity of the GW calculation due to the nonlocality and frequency dependence of the self-energy, it is usually difficult to analyze the self-energy in detail and sometimes it is even more difficult to get converged results [11–13]. The hydrogen atom is one of the few real systems where the exact eigenfunctions and energies are known analytically, and it is an ideal system for studying the self-screening problem because, for the $1s$ state, the error arises entirely from the correlation part of the self-energy. In this paper, we perform the GW calculation of the hydrogen atom using those exact wave functions and energies. We use the analytic form of both bound and continuum eigenfunctions, therefore, the calculation is free from the error coming from the incompleteness of the basis set, and detailed analysis of the self-energy is possible without any ambiguity. The standard LDA is known to yield a large self-interaction error of ∼7 eV in the ionization energy. Nelson *et al.* [14] performed the GW calculation of the hydrogen atom, and they obtained the self-energy of 0.21 eV starting

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from the exact eigenstates. We obtain a much smaller value of ≈0.02 eV, which is explained by the cancellation of the self-energy components with different angular momenta.

II. METHOD

Our starting point is the Hamiltonian of the isolated hydrogen atom (we use atomic units throughout this paper),

$$H = -\frac{1}{2}\nabla^2 + \frac{1}{r}. \quad (1)$$

The eigenfunctions of this Hamiltonian consist of discrete bound states and unbound states with continuum spectra. We decompose the eigenfunctions into radial and spherical parts as usual,

$$\psi_{nlm}(\mathbf{r}) = \phi_{nl}(r)Y_{lm}(\hat{r}). \quad (2)$$

Here, $\phi_{nl}(r)$ is normalized as $\int_0^\infty |\phi_{nl}(r)|^2 r^2 dr = 1$, and Y_{lm} is the spherical harmonics. The bound states with principal quantum number n have the eigenenergy $\epsilon_{nl} = -\frac{1}{2n^2}$. The analytic expression of $\phi_{nl}(r)$ can be found in standard textbooks.

The continuum eigenstates with energy ϵ are labeled by continuous variable $k = \sqrt{2\epsilon}$. Their analytic expression is [15]

$$\phi_{kl}(r) = c(k,l)\frac{(2kr)^l e^{-ikr}}{(2l+1)!}F\left[\frac{i}{k}+l+1,2(l+1),2ikr\right], \quad (3)$$

with $c(k,l)$ as the normalization constant,

$$c(k,l) = \sqrt{\frac{8\pi k}{1-e^{-2\pi/k}}}\prod_{p=1}^{l}\sqrt{p^2+\frac{1}{k^2}}, \quad (4)$$

and $F(\alpha,\gamma,z)$ is the confluent hypergeometric function. The continuum states are normalized as

$$\int_0^\infty \phi_{kl}(r)\phi_{k'l}(r)r^2 dr = 2\pi\delta(k-k'). \quad (5)$$

With these eigenstates, the completeness relation is written as

$$\delta(\mathbf{r}-\mathbf{r}') = \sum_{l=0}^{\infty}\left[\sum_n \phi_{nl}(r)\phi_{nl}(r') + \int_0^\infty \frac{dk}{2\pi}\phi_{kl}(r)\phi_{kl}(r')\right]$$
$$\times \sum_{m=-l}^{+l} Y_{lm}(\hat{r})Y_{lm}^*(\hat{r}'). \quad (6)$$

In the GW approximation [4–6], the self-energy is written as the product of the Green's function G and the screened Coulomb interaction W,

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \frac{-1}{2\pi i}\int_{-\infty}^{+\infty} G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega')d\omega'. \quad (7)$$

The screened Coulomb interaction W satisfies the equation $W = V + VPW$, where V is the bare Coulomb interaction and P is the polarization function calculated as

$$P(\mathbf{r},\mathbf{r}';\omega) = -i\int_{-\infty}^{+\infty} G(\mathbf{r},\mathbf{r}';\omega+\omega')G(\mathbf{r}',\mathbf{r};\omega')d\omega'. \quad (8)$$

The response function R is defined as

$$\begin{aligned} R(\omega) &= P(\omega) + P(\omega)VR(\omega) \\ &= [1 - P(\omega)V]^{-1}P(\omega), \end{aligned} \quad (9)$$

and with this R, W is also expressed as $W(\omega) = V + VR(\omega)V$.

In the G_0W_0 approach, the Green's function G appearing in Eqs. (7) and (8) is replaced by the noninteracting Green's function G_0. The polarization function then has the following form:

$$\begin{aligned} P(\mathbf{r},\mathbf{r}';\omega) = \sum_{\text{spin}}\sum_i^{\text{occ.}}\sum_j^{\text{unocc.}} \psi_i(\mathbf{r})\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')\psi_i^*(\mathbf{r}') \\ \times \left[\frac{1}{\omega-(\epsilon_j-\epsilon_i)+i\eta} - \frac{1}{\omega+(\epsilon_j-\epsilon_i)-i\eta}\right]. \end{aligned} \quad (10)$$

Here, $\psi_i(\mathbf{r})$ and ϵ_i are the wave functions and energies of the noninteracting Hamiltonian, and η is an infinitesimal. In this paper, we perform the G_0W_0 calculation with the exact eigenstates in Eqs. (2) and (3). The frequency integral appearing in Eq. (7) is evaluated by using the contour-integral technique [3,16] in which the contour is chosen to be along the imaginary frequency axis and the contribution from the poles of the Green's function is added separately. Thus, we need the polarization function along the imaginary frequency axis as well as the real axis.

Along the imaginary axis, we use the eigenfunction basis to calculate the self-energy. Due to the spherical symmetry of the system, the polarization P is expanded as

$$P(\mathbf{r},\mathbf{r}';i\omega) = \sum_{l,m}\sum_\mu \Phi_{\mu l}(r)P_{\mu l}(i\omega)\Phi_{\mu l}(r')Y_{lm}(\hat{r})Y_{lm}^*(\hat{r}'), \quad (11)$$

where

$$\Phi_{\mu l}(r) = \phi_{1s}(r)\phi_{\mu l}(r), \quad (12)$$

$$\begin{aligned} P_{\mu l}(i\omega) &= \frac{1}{4\pi}\left[\frac{1}{i\omega-\Delta_{\mu l}+i\eta} - \frac{1}{i\omega+\Delta_{\mu l}-i\eta}\right] \\ &= -\frac{1}{4\pi}\left[\frac{2\Delta_{\mu l}}{\omega^2+\Delta_{\mu l}^2}\right]. \end{aligned} \quad (13)$$

Here, $\Delta_{\mu l} = \epsilon_{\mu l} - \epsilon_{1s}$ and the factor $\frac{1}{4\pi}$ comes from $Y_{l=0}(\hat{r})Y_{l=0}^*(\hat{r}')$. We use greek letters to represent both bound and unbound states (i.e., $\mu = n,k$). In this expansion, P

is diagonal. We note that $P_{\mu l}$ is an expansion coefficient and is different from the matrix element of P in this basis due to the nonorthogonality of $\Phi_{\mu l}$ [i.e., $P_{\mu l}(i\omega) \neq \int \Phi_{\mu l}(r)Y_{lm}^*(\hat{r})P(\mathbf{r},\mathbf{r}';i\omega)\Phi_{\mu l}(r')Y_{lm}(\hat{r}')d^3r\,d^3r'$]. The response function in Eq. (9) is expanded similarly, but it has the off-diagonal coefficients $R_{\mu\nu l}$ ($\mu \neq \nu$). The matrix elements of the Coulomb interaction V in this basis are

$$\begin{aligned} V_{\mu\nu l} &= \langle\Phi_{\mu l}|V_l|\Phi_{\nu l}\rangle \\ &= \int \Phi_{\mu l}(r)V_l(r,r')\Phi_{\nu l}(r')r^2 r'^2 dr\,dr', \end{aligned} \quad (14)$$

where

$$V_l(r,r') = \frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}. \quad (15)$$

We discretize k and replace the integral over k by a discrete sum.

Along the real frequency axis, $\text{Im}\,P_{kl}(\omega) = -\frac{1}{4}\delta(\omega \pm \Delta_{kl})$ is a singular function of k, so instead of expanding P with the eigenfunction basis, we expand the Coulomb interaction by the spherical wave; using the expansion formula of the plane wave,

$$e^{i\mathbf{q}\cdot\mathbf{r}} = \sum_{l,m} 4\pi i^l j_l(qr)Y_{lm}(\hat{r})Y_{lm}^*(\hat{q}), \quad (16)$$

with $j_l(x)$ as the spherical Bessel function, the Coulomb interaction is expanded as

$$\begin{aligned} V(\mathbf{r}-\mathbf{r}') &= \frac{1}{(2\pi)^3}\int d^3q \frac{4\pi}{q^2}e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} \\ &= \sum_{l,m}\int_0^\infty dq\, V_l(q)j_l(qr)j_l(qr')Y_{lm}(\hat{r})Y_{lm}^*(\hat{r}'), \end{aligned} \quad (17)$$

with $V_l(q) = 8$. The matrix elements of the polarization function in this spherical-wave basis are calculated as

$$P_{qq'l}(\omega) = \sum_\mu A_{\mu l}(q)P_{\mu l}(\omega)A_{\mu l}(q'), \quad (18)$$

where

$$A_{\mu l}(q) = \int_0^\infty \Phi_{\mu l}(r)j_l(qr)r^2 dr. \quad (19)$$

In practice, we first calculate the imaginary part of $P_{qq'l}(\omega)$ and then generate the real part of $P_{qq'l}(\omega)$ via the Kramas-Kronig transformation. The contribution from the continuum states to $\text{Im}\,P_{qq'l}(\omega)$ can be calculated analytically as

$$\begin{aligned} \int_0^\infty \frac{dk}{2\pi} A_{kl}(q)&\text{Im}\,P_{kl}(\omega)A_{kl}(q') \\ &= -\frac{1}{4}\int_0^\infty \frac{dk}{2\pi} A_{kl}(q)\delta(\omega-\Delta_{kl})A_{kl}(q') \\ &= -\frac{1}{8\pi}\frac{A_{k_0 l}(q)A_{k_0 l}(q')}{k_0}, \end{aligned} \quad (20)$$

where $k_0 = \sqrt{2(\omega+\epsilon_{1s})}$ ($\omega > -\epsilon_{1s}$). Along the real axis, we discretize q.

Finally, the correlation part of the self-energy of the 1s state is calculated as

$$\langle\psi_{1s}|\Sigma^c(\omega)|\psi_{1s}\rangle = \frac{-1}{2\pi i}\sum_{l,\mu}\frac{2l+1}{4\pi}$$
$$\times \int_C d\omega' \frac{\langle\Phi_{\mu l}|V_l R_l(\omega')V_l|\Phi_{\mu l}\rangle}{\omega+\omega'-\epsilon_{\mu l}\pm i\eta}, \quad (21)$$

where $+(-)$ signs correspond to the unoccupied(occupied) states and C denotes the contour defined in Ref. [16].

The wave functions enter the calculation only through the Coulomb matrix $V_{\mu\nu l}$ in Eq. (14) and $A_{\mu l}(q)$ in Eq. (19). We calculate $V_{\mu\nu l}$ and $A_{\mu l}(q)$ analytically as performed by Yamagami and Takada [17].

In this paper, we concentrate on the self-energy and the quasiparticle energy of the 1s state ϵ_{1s}^{QP}. For the 1s state, the (bare) exchange self-energy exactly cancels out the Hartree term, therefore, ϵ_{1s}^{QP} is calculated as

$$\epsilon_{1s}^{QP} = \epsilon_{1s} + \langle\psi_{1s}|\Sigma^c(\epsilon_{1s}^{QP})|\psi_{1s}\rangle. \quad (22)$$

Since the exact electron removal energy should be equal to ϵ_{1s}, the true self-energy should satisfy $\langle\psi_{1s}|\Sigma^c(\epsilon_{1s})|\psi_{1s}\rangle = 0$. Therefore, we use $\langle\psi_{1s}|\Sigma^c(\epsilon_{1s})|\psi_{1s}\rangle$ as a measure of the error in the GW approximation.

The calculations require two convergence parameters, namely, the principal quantum number cutoff $n_{\max}$ and the angular momentum cutoff $l_{\max}$. In this paper, we set $n_{\max} = 10$ and vary $l_{\max}$ up to $l = 5$.

III. RESULTS AND DISCUSSION

Figure 1 shows the correlation part of the self-energy at $\omega = \epsilon_{1s}$, the 1s state, by changing $l_{\max}$ up to $l = 5$. It can be seen that, as $l_{\max}$ goes from $l = 0$ to $l = 1$, the error of the self-energy or the quasiparticle energy drastically reduces by around 0.6 eV, and by increasing $l_{\max}$, the self-energy decreases monotonically. The self-energy converges slowly with respect to $l_{\max}$, which is reminiscent of a similar problem in GW calculations associated with summing over unoccupied states [11–13]. Our estimated value for $l_{\max} \to \infty$ by extrapolation is 0.02 ± 0.01 eV.

TABLE I. Contribution of the selected states to the correlation part of the self-energy [Eq. (23)] at $\omega = \epsilon_{1s}$. Energies are in eV.

$l = 0$	1s	$+1.09$
	2s	-0.05
	Unbound	-0.23
	Total	$+0.78$
$l = 1$	2p	-0.09
	3p	-0.02
	Unbound	-0.46
	Total	-0.60
$l = 2$	3d	$\sim -10^{-4}$
	Unbound	-0.10
	Total	-0.10

As can be seen in Eq. (21), we can divide the self-energy into the different (μ,l) components as

$$\langle\psi_{1s}|\Sigma^c(\omega)|\psi_{1s}\rangle = \sum_{l=0}^{l_{\max}}\sum_{\mu}\Sigma_{\mu l}^c(\omega). \quad (23)$$

Each component $\Sigma_{\mu l}^c(\omega)$ shows the contribution of each eigenstate to the self-energy through the Green's function appearing in Eq. (7), but the screened interaction W and the polarization function P contain the contributions of all states. In Table I, the values of $\Sigma_{\mu l}^c(\omega = \epsilon_{1s})$ are shown for selected states. Only the 1s component gives a positive contribution, and all other unoccupied states give a negative contribution; the $l = 0$ component contains the large error of $+0.78$ eV in total, which mainly comes from the 1s contribution $\Sigma_{1s}^c(\omega)$, but most of the error is canceled by the contribution of the states with higher l, especially the states with $l = 1$. This shows that the occupancy and symmetry of the states that form the Green's function in Eq. (7) play an important role in determining the self-energy.

To analyze this point further, in Fig. 2, we plot each l component of the self-energy, i.e., $\Sigma_l^c(\omega) = \sum_\mu \Sigma_{\mu l}^c(\omega)$ as
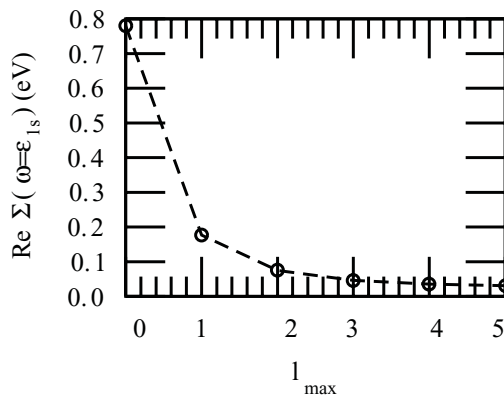

FIG. 1. The correlation part of the self-energy [Eq. (21)] of the 1s state at $\omega = \epsilon_{1s}$ for various $l_{\max}$'s calculated with $n_{\max} = 10$. Energies are in eV. The line is a guide for the eye.
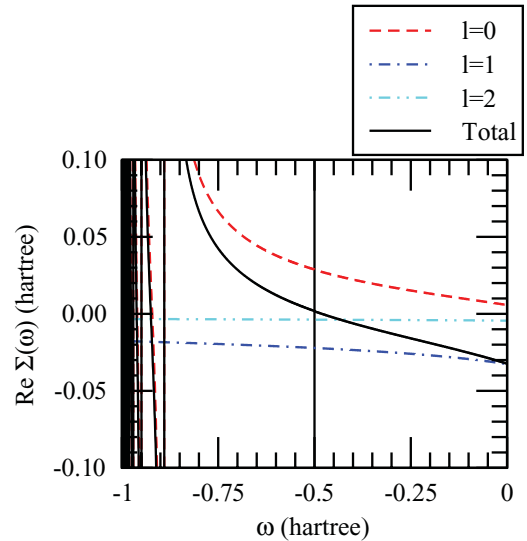

FIG. 2. (Color online) The l components of the correlation part of the self-energy up to $l = 2$ as a function of frequency. Only the real parts are shown.

a function of frequency. It can be seen that only the $l = 0$ component has peaks below ≈ -0.9 hartree, which pulls up the real part of the self-energy and explains the large positive contribution of this component. The other l components do not have the peaks there and are negative in the whole region in Fig. 2 in accordance with the results in Fig. 1 and Table I.

This tendency can be qualitatively understood by noting that, for the low-energy region, the response function $R_l(\omega)$ can be written as a sum of discrete poles as

$$R_l(\omega) = \sum_j R_l^j \left[\frac{1}{\omega - \Omega_{jl} + i\eta} - \frac{1}{\omega + \Omega_{jl} - i\eta} \right], \quad (24)$$

where Ω_{jl} are the poles of $R_l(\omega)$, which are essentially the transition energy to the bound states, Δ_{nl} in Eq. (13), modified by the Coulomb interaction. With this $R_l(\omega)$, $\Sigma_{\mu l}^c(\omega)$ for a given (μ, l) state is calculated as

$$\Sigma_{\mu l}^c(\omega) = -\frac{1}{2\pi i} \sum_j \int d\omega' \frac{2l+1}{4\pi} \frac{\langle \Phi_{\mu l} | V_l R_l^j V_l | \Phi_{\mu l} \rangle}{\omega + \omega' - \epsilon_{\mu l} \pm i\eta}$$

$$\times \left[\frac{1}{\omega' - \Omega_{jl} + i\eta} - \frac{1}{\omega' + \Omega_{jl} - i\eta} \right]$$

$$= \begin{cases} \sum_j \frac{1}{4\pi} \frac{\langle \Phi_{1s} | V_0 R_0^j V_0 | \Phi_{1s} \rangle}{\omega - (\epsilon_{1s} - \Omega_{j0}) - i\eta}, & (\mu, l) = 1s, \\ \sum_j \frac{2l+1}{4\pi} \frac{\langle \Phi_{\mu l} | V_l R_l^j V_l | \Phi_{\mu l} \rangle}{\omega - (\epsilon_{\mu l} + \Omega_{jl}) + i\eta}, & (\mu, l) \neq 1s. \end{cases} \quad (25)$$

Thus, the positions of the poles in the self-energy, which give the peak structure, depend on the occupancy of each state in G_0. The peaks below around -0.9 hartree in $\Sigma_{l=0}^c(\omega)$ in Fig. 2 are due to the poles of the occupied $1s$ component $\Sigma_{1s}^c(\omega)$ located at $\omega = \epsilon_{1s} - \Omega_{jl=0}$, where $\Omega_{jl=0} \sim 0.4$ hartree. For the unoccupied states, Eq. (25) gives the poles $\omega = \epsilon_{\mu l} + \Omega_j$, which are located in the higher-energy region (outside the energy range in Fig. 2), and these explain the negative contribution for the $l > 0$ components.

The amplitude of the self-energy is determined by the matrix element $\langle \Phi_{\mu l} | V_l R_l^j V_l | \Phi_{\mu l} \rangle$, the numerator of Eq. (25). As shown in Table I, for this system, the dominant error is caused by the $1s$ component Σ_{1s}^c, which involves the large self-overlap of the $1s$ state $\langle \psi_{1s} \psi_{1s} | V_l R_l^j V_l | \psi_{1s} \psi_{1s} \rangle$. In this system, however, this large error is canceled by the contributions from the unoccupied states, especially unbound states with $l = 1$. This shows that the unbound continuum states have an important contribution to the self-energy. The importance of the unbound states is also reported by Yamagami and Takada in their paper on the helium atom [17].

To further analyze the effect of unbound states, in Fig. 3, we show the self-energy calculated completely without the continuum states, i.e., neither in the Green's function nor in the polarization function. In this case, the states with $l > 1$ affect the self-energy little due to the very small overlap with the $1s$ state, and the resulting self-energy contains a large error of $+0.59$ eV. This result shows that the continuum states affect both the Green's function in the self-energy, as shown in Table I, and the polarization function. To see the effect of the continuum states on the polarization function, in Figs. 4(a) and 4(b), we plot the polarization function $P_{qq'l}(\omega)$ defined in Eq. (18). The imaginary part of the polarization [Fig. 4(a)] consists of two parts, namely, discrete peaks below
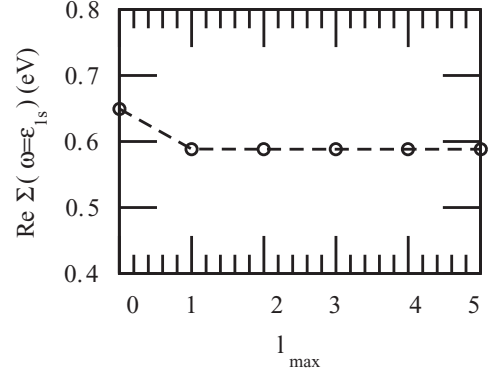

FIG. 3. The correlation part of the self-energy [Eq. (21)] at $\omega = \epsilon_{1s}$ for various l_{max}'s calculated including only the bound states up to $n_{max} = 10$. Energies are in eV. The line is a guide for the eye.

$\omega = \frac{1}{2}$ hartree due to the excitation to the bound states and the continuum spectra due to the continuum states. The latter contribution, as seen in Fig. 4(b), increases the real part of the polarization for small ω, and this affects the screened interaction W. Without the continuum states, the static ($\omega = 0$) value of the polarization is small for $l > 0$, indicating that these bound states do not contribute much to the screening process.

The importance of the continuum states may also be understood by considering the Thomas-Reiche-Kuhn or
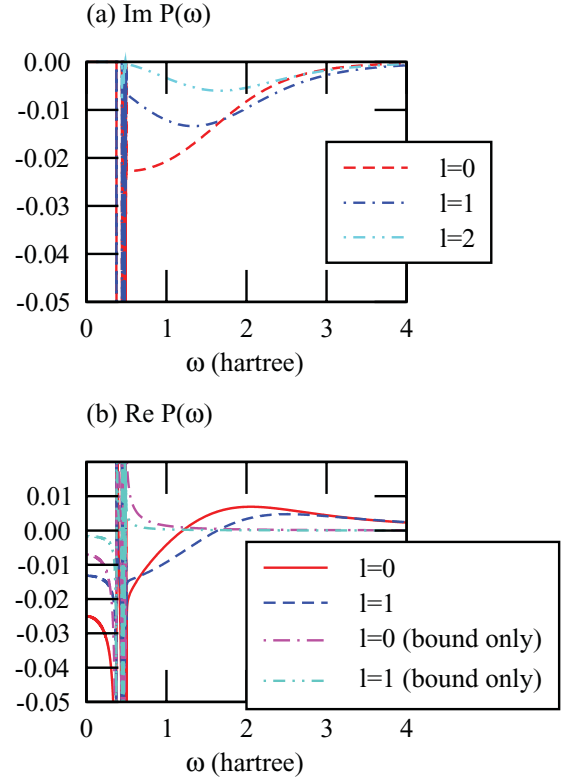

FIG. 4. (Color online) (a) The imaginary part of $P_{qq'l}(\omega)$ at $q = q' = 4$. (b) The real part of $P_{qq'l}(\omega)$ up to $l = 1$. The results obtained by including only the bound states are also shown for comparison.
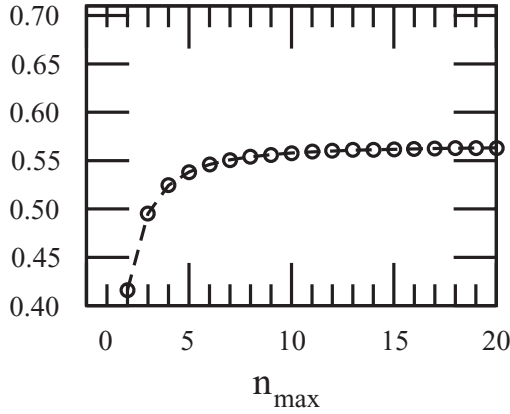
FIG. 5. The f-sum rule [the left-hand side of Eq. (26)] calculated with only the bound eigenstates up to $n = n_{max}$. The line is a guide for the eye.

f-sum rule for an isolated system [18–20],

$$2\sum_N (E_N - E_0)|\langle N|x_i|0\rangle|^2 = 1 \qquad (26)$$

for $x_i = x, y, z$, which can be derived by considering the commutation relation $[x_i, p_j] = i\delta_{ij}$. Here, $|0\rangle$ is the ground state of the system, and N runs over the whole eigenstate with eigenenergy E_N. In Fig. 5, we show the contribution of the bound states to the left-hand side of Eq. (26) as a function of the principal quantum number cutoff n_{max}. The bound states account only for 0.56 of the total, and the contribution of the unbound states is as large as ≈ 0.43, which is also confirmed by a direct calculation using the wave functions in Eq. (3). Noting that this quantity is essentially determined by the overlap between the 1s state and the unoccupied p states, this large contribution of the continuum states also shows the importance of the continuum states with $l = 1$ in the self-energy and the polarization as shown in Table I and Fig. 4.

The error of ≈ 0.02 eV in the 1s removal energy, obtained in this paper, is unexpectedly small. This may be partly due to the fact that we use the exact hydrogen wave functions, which are free from the self-interaction effect. Indeed, when the LDA wave functions, which contain the self-interaction error, are used, the error becomes much larger as found by Nelson *et al.* [14]. Similar results were obtained by Fernandez [21] in the GW calculation of a simple model system. Our value of 0.02 eV, however, is considerably smaller than the

error of 0.21 eV obtained by Nelson *et al.*, who also used the exact wave functions in their calculations.

Finally, we discuss the implication of our results; our finding is that, the dominant source of the error in the self-energy for the 1s state is the term containing the overlap between itself, namely, the term $\Sigma_{1s}(\omega) \propto \langle\psi_{1s}\psi_{1s}|W^c|\psi_{1s}\psi_{1s}\rangle$; however, unlike the self-interaction appearing in the LDA, due to the frequency dependence or dynamical nature of the screening interaction, most of this self-screening error is canceled by the negative contribution of the components with different symmetries, especially continuum states with $l = 1$, which have large overlap matrix elements with the 1s state. Although, in the general case, the self-energy is also affected by many other parameters, we expect this kind of cancellation would still occur in other systems. However, for more localized states, for example, d orbitals in transition metals or semicore states, the contribution of the term including the self-overlap (i.e., $\langle\psi_d\psi_d|W^c|\psi_d\psi_d\rangle$) is very large, and it pushes up their energy level significantly; incomplete cancellation of this contribution may be the main reason that the G_0W_0 approach cannot describe the localized states well. This point will be investigated in future papers.

IV. CONCLUSIONS

To summarize, we have performed the self-energy calculation of the hydrogen atom using the analytic form of the exact eigenstates and have found the very small error of the electron-removal energy for this system, which is explained by the cancellation of the self-screening error due to the different signs of the self-energy components with different angular momenta.

We have also found the important contribution of the continuum states to the self-energy. Accurate treatment of unoccupied states within a finite basis set is a significant problem of GW calculations [22–26], and we have shown that the f-sum rule would be one useful measure to check the quality of a given basis set.

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