Comparison between the Full Frequency Integration and the GPP Model in ab-initio GW Calculation of Na Clusters

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An ab initio calculation of electronic excitation energies based on the GW approximation is performed by using the all-electron mixed-basis approach. The generalized plasmon-pole (GPP) model is used to determine the electron self-energy and the results are compared with our previous results using the full frequency integration (S. Ishii et al., Phys. Rev. B 63 155104 (2001)). It is found that the two methods with and without the GPP model agrees well in the case of sodium clusters.

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The state-of-art Hedin's GW approximation (GWA) is one of the best ab initio theory introduced in the framework of the quantum field theory. It is able to predict accurately electronic excitation energies, which is not be handled with the standard approximation, such as the local density approximation (LDA), based on the density functional theory. The ab-initio GW calculation was first performed by Hybertsen and Louie for typical semiconductors such as silicon and diamond and succeeded in reproducing the band gap correctly. However, the electron self-energy operator in the GWA is not local and frequency dependent. In order to determine it, one must first calculate the dielectric response function, which is also nonlocal in space and frequency dependent, and then perform a frequency integration, which is generally quite heavy. Because of this reason, it has been a difficult task to perform an ab-initio GW calculation directly due to the limitations of the computational resources unless one introduces a simplified model or empirical parameters. There are many proposed dielectric response functions such as Levine and Louie function, Lindhard's function, and so on. One of the most typical model mostly used in the GW calculation is the generalized plasmon-pole (GPP) model. In the GW calculation using the GPP model, one need not evaluate the frequency dependence of dielectric function but evaluate only static dielectric constants numerically and expand them to finite frequencies by a simple assumption and using a sum rule. However, as pointed out by Godby et al., the GPP model breaks down at the order of the plasma frequency.

Recently Ishii et al. performed an ab-initio all-electron GW calculation by carrying out the full \( \omega \) integration without relying on any models or empirical parameters, and succeeded in obtaining accurate absolute values of ionization potential and electron affinity of small sodium clusters. In the present paper, we implement the GPP model to our source code and apply this model again to the same sodium clusters studied in Ref. 11. The aim of the present paper is to compare and discuss two results with and without the GPP model.

We employ the all-electron mixed-basis approach, which is a natural extension of the pseudopotential approach to take the core electrons fully into account. In this approach, the wave function is expanded by both plane waves and atomic orbitals. Typically wave functions of valence and unoccupied levels are primarily represented by plane waves and those of core levels are represented by the atomic orbitals of isolated atoms. In the present calculation we employed Herman-Skillman's numerical atomic code on a radial logarithmic mesh, which allows an accurate description in the vicinity of nuclei. The present approach have been successfully applied to many ab-initio calculations and molecular dynamics simulations. In the present calculation of sodium clusters, we employ only AO's having 1s, 2s, and 2p core characters. The result is changed only little when we incorporate 3s valence AO's.

In the GW approximation, the self-energy operator \( \Sigma \) is taken to be the first-order term in an expansion with respect to the screened Coulomb interaction \( W \) and is given by

\[
\Sigma(r, r'; \omega) = i \int d\omega' G(r, r'; \omega + \omega') W(r, r'; \omega') e^{i\omega'}. 
\]

The screened Coulomb interaction \( W \) is usually calculated within the random phase approximation (RPA) and represented in terms of the RPA dielectric response function \( \varepsilon(r, r'; \omega) \) and the bare Coulomb interaction \( v(r - r') = 1/|r - r'| \). That is, its Fourier transform, \( W_{G, G'}(q, \omega) \), is given by

\[
W_{G, G'}(q, \omega) = \epsilon^{-1}_{G, G'}(q, \omega) v(q + G').
\]

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two parts. One is the Fock exchange energy operator:

$$
\Sigma_x(r, r') = \frac{i}{2\pi} v(r - r') \int \frac{e^{i\omega \cdot n} G(r, r'; \omega') d\omega'}{|r - r'|}.
$$

(2)

The diagonal part of $\Sigma_x$ in the LDA orbital basis can be written as

$$
\Sigma_{x,n} = \langle \psi_n(r) | \Sigma_x(r, r') | \psi_n(r') \rangle
= - \int dr \int dr' \sum_m \psi_m^*(r) \psi_m(r') \frac{\psi_m^*(r') | \psi_n(r') \rangle}{|r - r'|}.
$$

(3)

Therefore, to evaluate $\Sigma_{x,n}$, one need not perform the $\omega$ integration numerically. Another term corresponds to the correlation energy operator

$$
\Sigma_c(r, r'; \omega) = \frac{i}{2\pi} \int d\omega' e^{i\omega \cdot n} G(r, r'; \omega + \omega') \times [W(r, r'; \omega') - \langle \psi_n(r) | \Sigma_x(r, r') | \psi_n(r') \rangle],
$$

(4)

and its diagonal matrix element becomes

$$
\Sigma_{c,n} = \langle n, k | \Sigma_c(r, r'; \omega) | n, k \rangle
= \sum_{n', k} \langle n', k | e^{-i(q+G) \cdot r'} | n', k - q \rangle
\times \langle n', k - q | e^{i(q-G') \cdot r'} | n, k \rangle
\times i \int_0^{\infty} \frac{d\omega'}{2\pi} \left\{ W_{G,G'}(q, \omega') - \delta_{G,G'} v(q + G) \right\}
\times \frac{1}{\omega + \omega' - E_{n', k - q} - i\delta_{n', k - q}}
+ \frac{1}{\omega - \omega' - E_{n', k - q} - i\delta_{n', k - q}}
$$

(5)

with the help of $W(\omega) = W(-\omega)$. Here $\delta_{n,n'}$ denotes positive and negative infinitesimal numbers, respectively, for occupied and unoccupied levels. To evaluate $\Sigma_{c,n}$, one has to perform, in principle, the $\omega$ integration.

On the other hand, the GPP model assumes that $\text{Im} \varepsilon_{G,G'}^{-1}(\omega)$ has a single peak at the frequency of $\omega_{G,G'}$ (see below). If one employs the GPP model, eq. (5) is replaced by

$$
\Sigma_{c,n} = - \sum_m \sum_{q, G, G'} \langle m, k | e^{i(q+G) \cdot r'} | m, k - q \rangle
\times \langle m, k - q | e^{-i(q+G') \cdot r'} | m, k \rangle
\times \frac{\Omega_{G,G'}^2(q)}{(E - E_{m,k,q})^2 - \omega_{G,G'}^2(q)} v(q + G')
+ \frac{1}{2} \sum_m \sum_{q, G, G'} \langle nk | e^{i(q+G) \cdot r} | m, k - q \rangle
\times \langle m, k - q | e^{-i(q+G') \cdot r} | n, k \rangle
\times \frac{\Omega_{G,G'}^2(q)}{\omega_{G,G'}(q) [E - E_{m,k,q} - \omega_{G,G'}(q)]} v(q + G').
$$

(6)

Here $\Omega_{G,G'}(q)$ and $\omega_{G,G'}(q)$ are determined by the generalized $f$-sum rule and given by using the plasma frequency $\omega_p$ and the charge density $\rho$:

$$
\Omega_{G,G'}^2(q) = \omega_p^2 \frac{(q + G) \cdot (q + G')}{|q + G|^2} \frac{\rho(G - G')}{\rho(0)},
$$

(7)

$$
\omega_{G,G'}(q) = \frac{\Omega_{G,G'}^2(q)}{\delta_{G,G'} - \varepsilon_{G,G'}^{-1}(q, \omega = 0)}.
$$

(8)

Therefore, under this approximation, one can totally skip the frequency integration in the evaluation of the self-energy operator.

Our purpose is to compare the explicit values of eq. (5) with those of eq. (6) for several small sodium clusters. The technical details of the present calculation is the same as in Ref. 11. The structures of the sodium clusters are completely the same as those studied in Ref. 11. When we calculate eq. (5), we perform the summation with respect to $n^\prime$ only over valence levels. Similarly, when we calculate eq. (7), we use the valence charge density only. This approximation is good enough at least for $\Sigma_{c,n}$. In the calculation of eq. (6), the denominator may become very close to zero for a special combination of $(G, G^\prime, q)$ accidentally. To avoid such singularity, here we take average of the integrand with respect to $\omega$ in the interval $(\omega - \delta, \omega + \delta)$, and replace it with a simple logarithmic function.

To calculate eq. (5) the interval and area of integration with respect to $\omega$ is taken to be the same as in Ref. 11.

Figure 1 shows the $\Sigma_{c,n}$ of the (a) HOMO and (b) LUMO levels for the sodium dimer calculated by employing either the GPP model (crosses) or the numerical integration (open circles). Crosses show the results with the GPP model and open circles show those with the numerical integration.

**Fig. 1** Correlation term of the self-energy ($\Sigma_{c,n}$) at the (a) HOMO and (b) LUMO levels for a sodium dimer obtained with and without the GPP model as a function of the number of the G-vectors representing the non-local interactions. Crosses show the results with the GPP model and open circles show those with the numerical integration.
Table 1  Cluster size dependence of the correlation term of the self-energy ($\Sigma_{c,n}$) for sodium clusters calculated by employing either the GPP model or the numerical integration.

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<tr>
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<th>Numerical integration</th>
<th>GPP model</th>
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<tbody>
<tr>
<td>$\text{Na}_2$ HOMO</td>
<td>$-0.73\text{ eV}$</td>
<td>$-0.71$</td>
</tr>
<tr>
<td>LUMO</td>
<td>$-0.66$</td>
<td>$-0.66$</td>
</tr>
<tr>
<td>$\text{Na}_4$ HOMO</td>
<td>$-1.01$</td>
<td>$-0.90$</td>
</tr>
<tr>
<td>LUMO</td>
<td>$-1.35$</td>
<td>$-1.23$</td>
</tr>
<tr>
<td>$\text{Na}_6$ HOMO</td>
<td>$-0.86$</td>
<td>$-0.69$</td>
</tr>
<tr>
<td>LUMO</td>
<td>$-1.53$</td>
<td>$-1.49$</td>
</tr>
<tr>
<td>$\text{Na}_8$ HOMO</td>
<td>$-0.85$</td>
<td>$-0.70$</td>
</tr>
<tr>
<td>LUMO</td>
<td>$-1.40$</td>
<td>$-1.25$</td>
</tr>
</tbody>
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circles). In both methods, 645 $G$-vectors are used to represent the nonlocal interactions and to achieve a good convergence within 0.1 eV in the calculation of eqs. (4) and (5). We find the tendency that the more the number of $G$-vectors, the larger the absolute value of $\Sigma_{c,n}$. This means that the space nonlocality is essential for the self-energy. Both methods agree very well within the order of 0.1 eV. Hence, the GPP model is a very good approximation particularly for the dimer.

Table 1 shows the comparison of the results obtained by the GPP model and numerical integration for all the clusters studied in the present calculation. From this table, it is seen that the results obtained by the GPP model reproduce those by the numerical integration within the error of at most 0.15 eV. This is comparable to our estimation error (0.1 eV) for the quasiparticle energies when we use the full $\omega$ integration.

Although the absolute values of the HOMO and LUMO energies shift a little shallower when we use the GPP model, the energy difference between the HOMO and LUMO levels remains almost unchanged regardless of the method used. One can see that, as the cluster size increases, the discrepancy between the absolute (HOMO, LUMO) energies obtained in the two methods tends to be a little larger.

As mentioned above, the GPP model assumes a $\delta$-function type excitation such that excitations occur at the energy of $\tilde{\omega}_{G,G'}(q, \omega)$. In fact, the contribution from the detail local structures of $W$ is not important as pointed out in Ref. 5. However, eq. (6) does not always have a real solution for all combinations of $G$, $G'$, and $q$. Sometimes, it leads to imaginary numbers of $\tilde{\omega}_{G,G'}(q)$, which means breakdown of the GPP model. According to Ref. 5, we simply ignore such combinations of $G$, $G'$, and $q$. If there are so many such combinations, the GPP model may become worse. In the present calculation, we found that such cases are about 1/3 to 1/2 of the total combinations. It is surprising, however, that the GPP model nevertheless reproduces the results obtained by numerical integration fairly well.

In summary, we implemented the GPP model in the all-electron mixed-basis code and applied it to the sodium clusters. The GPP model reproduces well the results of the full numerical integration of the correlation term of the electron self-energy in particular for sodium dimer, although there are many nonlocal ($G$, $G'$) combinations that make the GPP model worse.

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REFERENCES