Optical Properties of Alkali-Earth Atoms and Na$_2$ Calculated by $GW$ and Bethe–Salpeter Equations

Kaoru Ohno*

Department of Physics, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

Abstract

Starting from the $GW$ approximation (GWA) beyond density functional theory and solving the eigenvalue problem associated with the Bethe–Salpeter equation which accounts for the excitonic effect, I have determined optical properties of isolated Be, Mg and Ca atoms and Na$_2$. In the representation of single electron wave functions, I have used the all-electron mixed basis approach in which both plane waves and atomic orbitals are used as a basis set. The resulting quasiparticle energies and optical absorption spectra are compared with available experimental data.

Key words: first principles, quasiparticle energy, optical absorption spectra, perturbation theory, ladder diagram

* Corresponding author. Tel.: +81-45-339-4254; Fax: +81-45-338-3020
Email address: ohno@ynu.ac.jp (Kaoru Ohno).
Quasiparticle energy spectra of real materials can be calculated accurately by means of the $GW$ approximation (GWA) [1–3] which treats the first-order contribution to the self-energy (for the one-particle Green’s function $G$) with respect to the dynamically screened Coulomb interaction $W$ given in the random-phase approximation (RPA).

In the GWA, the quasiparticle energies $\varepsilon_{n}^{\text{QP}}$ and wave functions $\psi_{n}(\mathbf{r})$ are obtained by solving

\begin{equation}
(T + V_{\text{ext}} + V_{H})\psi_{n}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{n}^{\text{QP}})\psi_{n}(\mathbf{r}') = \varepsilon_{n}^{\text{QP}}\psi_{n}(\mathbf{r}),
\end{equation}

and

\begin{equation}
\Sigma(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}' ; \omega + \omega') W(\mathbf{r}, \mathbf{r}' ; \omega') e^{i\eta\omega'},
\end{equation}

where $T$, $V_{\text{ext}}$, $V_{H}$, and $\Sigma$ are the kinetic energy operator, external potential, Hartree potential, and electron self-energy containing the effect of exchange-correlation between electrons, respectively; $\eta$ is a positive infinitesimal number. $W$ is the dynamically screened Coulomb interaction expressed symbolically as $W = \varepsilon^{-1}U$ in the random phase approximation (RPA), where $U$ is the bare Coulomb interaction and $\varepsilon$ is the dielectric function $\varepsilon = 1 - 4\pi P$ (and $P = -iGG$ is the polarizability). Here the generalized plasmon pole model (GPP) [2] is used to evaluate the self-energy. The one-particle Green’s function $G$ is given by

\begin{equation}
G(\mathbf{r}, \mathbf{r}' , \omega) = \sum_{n'} \frac{\psi_{n'}(\mathbf{r})\psi_{n'}^{*}(\mathbf{r}')} {\omega - \varepsilon_{n'} - i\delta_{n'}},
\end{equation}

where $\delta_{n'} = 0^{+}$ for $\varepsilon_{n'} < \mu_{F}$ and $\delta_{n'} = 0^{-}$ for $\varepsilon_{n'} > \mu_{F}$, provided that $\mu_{F}$ is the Fermi energy. Conventionally $\psi_{n'}(\mathbf{r})$ and $\varepsilon_{n'}^{\text{QP}}$ have been replaced by the LDA wavefunctions and the LDA energy eigenvalues $\varepsilon_{n'}^{\text{LDA}}$, Then, quasi-particle energies are obtained in terms of first-order perturbation theory as

\begin{equation}
\varepsilon_{n}^{\text{QP}} \approx \varepsilon_{n}^{\text{LDA}} + \int d\mathbf{r} \int d\mathbf{r}'\psi_{n}^{*}(\mathbf{r})[\Sigma(\mathbf{r}, \mathbf{r}' , \varepsilon_{n}^{\text{QP}}) - \mu_{F}^{\text{LDA}}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')]\psi_{n}(\mathbf{r}').
\end{equation}

So far, many calculations with this GWA on ab initio level have been performed for variety of crystals and surfaces [4]. Recently, we have calculated quasi-particle energy spectra of small alkali-metal clusters [5,6] as well as small silicon clusters [7], by using our GW code implemented on the all-electron mixed basis approach [4–10], in which single particle wave functions are expanded with both plane waves (PW’s) and atomic orbitals (AO’s).

It has been recognized that spectroscopic properties involving two-particle
excitations should be determined still beyond the GWA, i.e., by evaluating
accurately the two-particle Green’s function [4]. In 1966, Sham and Rice [11]
solved the Bethe–Salpeter (BS) equation approximately to derive the effective
mass equation for bound excitons. The calculation of optical absorption
spectra of real materials in this approach requires an extremely heavy com-
putational load, and has been performed rather recently for Na$_4$ [12], Si$_n$H$_{2n}$
[13], a conjugate polymer [14], Si crystal [15] and so forth.

For isolated atoms and clusters, however, there is a specific issue which should
be addressed in the calculations of quasiparticle spectra. This is related to
the existence of continuum states in the excitation spectra above the vacuum
level. This continuum states are associated with the free electron states ex-
tended infinitely in space. Since all excited states (of isolated atoms and
clusters) above the vacuum level are embedded in this continuum, they are
not the true bound states but the resonance states having a finite life-time and
decaying to the free electron states. That is, a peak in the density of states
concerning to a resonance state is no more a sharp peak but broadened.
Correspondingly, the imaginary part of the quasiparticle energy is large and
the quasiparticle wavefunction is spatially more extended than the LDA wave-
functions. This statement is true even for the states under the vacuum level if
they are near the vacuum level. For the states near or above the vacuum level,
off-diagonal elements of the GW self-energy become important, and the GW
wavefunctions should be used instead of the LDA wavefunctions. Therefore,
for these states, it is necessary to diagonalize the full GW matrix to determine
the GW wavefunctions correctly. This procedure is particularly important for
the alkali-earth atoms such as Be, Mg and Ca, because they are the so-called
“negative affinity system”, i.e., their affinity level is located above the vacuum
level. Unfortunately, this fact has been often ignored in the previous studies
and must be cured and reflected onto optical properties of isolated atoms and
clusters.

In order to describe well not only core and bound states but also spatially
extended states like plane-wave states in a sufficiently large supercell with a
moderate number of basis functions, it is preferable to introduce a mixed-
basis representation which adopts both localized atomic orbitals and plane
waves as a basis set. The aim of the present study is to use the all-electron
mixed basis approach and calculate optical absorption spectra of alkali-earth
atoms and small sodium cluster by means of the BS equation starting from a
sophisticated GW calculation with off-diagonal elements in the self-energy.

The excitonic effect in the optical absorption spectra can be taken into account
by summing the electron-hole ladder diagrams, which become important in
particular at short distances, in the two-particle Green’s function. This can
be formulated by using the functional derivative of the electron self-energy
$U^\text{Hartree} + \Sigma^{GW}$ with respect to the one-particle Green’s function $G$. Thus
derived equation is the BS equation for the two-particle Green’s function, 
\[ S(1, 1'; 2, 2') = S_0(1, 1'; 2, 2') + S_0(1, 1'; 3, 3')\Xi(3, 3'; 4, 4')S(4, 4'; 2, 2'). \quad (5) \]

Here, \( S_0(1, 1'; 2, 2') = G(1', 2')G(2, 1) \) is the unperturbed function, in which the disconnected term \(-G(1, 1')G(2, 2')\) is excluded. (The notation \( G(1, 2) = G(\mathbf{r}_1, \mathbf{r}_2; t_1 - t_2) \) is used to express the one-particle Green’s function.) The interaction kernel \( \Xi \), which stands for the irreducible electron-hole interaction, is determined by \( \Xi = \delta(U^{\text{Hartree}} + \Sigma^{GW})/\delta G \) and contains two different contributions

\[ \Xi(1, 1'; 2, 2') = -i\delta(1, 1')\delta(2, 2')U(1, 2) + i\delta(1, 2)\delta(1', 2')W'(1, 1'), \quad (6) \]

where \( U(1, 2) = 1/|\mathbf{r}_1 - \mathbf{r}_2| \) comes from the functional derivative of the Hartree term \( U^{\text{Hartree}} \), and \(-W'(1, 1')\) represents the screened Coulomb attraction coming from the functional derivative of the GW self-energy \( \Sigma^{GW} \).

To solve (6), one has to invert a four-point function \( I = S_0\Xi \), where \( I \) is the identity operator. Strinati [16] derived a simplified eigenvalue equation which can be used to bypass the matrix inversion of the BS equation. Strinati treated positive frequency part only. Rohlffing and Louie [13] applied the Strinati scheme combined with the generalized plasmon-pole model. Albrecht et al. derived and applied a similar eigenvalue equation with static approximation (they treated negative frequency part as well). All these authors have used approximately the dynamically screened interaction \( W \) for the kernel \( W' \). This approximation is first used by Strinati [16] and is equivalent to neglecting the term \( G\delta W/\delta G \) in \( \delta\Sigma/\delta G \).

The full matrix appearing in the BS equation has a form

\[
H = \begin{pmatrix} 
D + X & 0 & 0 & X & \delta + \xi & 0 & 0 & \xi \\
0 & D & 0 & 0 & 0 & 0 & \delta & 0 \\
0 & 0 & D & 0 & 0 & \delta & 0 & 0 \\
X & 0 & 0 & D + X & \xi & 0 & 0 & \delta + \xi \\
-\delta^* - \xi^* & 0 & 0 & -\xi^* & -D^* - X^* & 0 & 0 & -X^* \\
0 & 0 & -\delta^* & 0 & 0 & -D^* & 0 & 0 \\
-\xi^* & 0 & 0 & -\delta^* - \xi^* & -X^* & 0 & 0 & -D^* - X^* 
\end{pmatrix}.
\]
where the first four and last four columns correspond, respectively, to the positive and negative frequency parts. The columns in each $4 \times 4$ submatrix correspond to the different spin states of the electron-hole pair (i.e., “exciton”): the four columns correspond in turn to up-up, up-down, down-up and down-down spin states. The matrix $D$ represents a direct term given by

$$D_{vc} = (\varepsilon_c^{QP} - \varepsilon_v^{QP})\delta_{vc} - W_{vc},$$

where $\varepsilon_c^{QP}$ and $\varepsilon_v^{QP}$ are the conduction and valence quasiparticle energies, respectively. The matrix $X$ represents an exchange term including also $-G\delta W/\delta G$. The $\delta$ and $\xi$ denote the corresponding off-diagonal parts, $\delta_{vc} = -W_{vc}$ and $\xi_{vc} = X_{vc}$. The dynamically screened Coulomb interaction $W$ is composed of two terms: the bare Coulomb term $U$ and the correlation term $S = W - U$.

It is a simple algebra to show that the matrix (7) is decomposed into four block-diagonal matrices; one has the form

$$\begin{pmatrix}
D + 2X & \delta + 2\xi \\
-\delta - 2\xi & -D - 2X
\end{pmatrix}$$

corresponding to the singlet exciton, and the other three have the form

$$\begin{pmatrix}
D & \delta \\
-\delta & -D
\end{pmatrix}$$

corresponding to the triplet exciton. Thus the BS eigenvalue equation $HA(\Omega) = \Omega A(\Omega)$ can be formally solved to yield

$$\Omega_{\pm}^{\text{singlet}} = \pm \sqrt{|D + 2X|^2 - |\delta + 2\xi|^2},$$

$$\Omega_{\pm}^{\text{triplet}} = \pm \sqrt{|D|^2 - |\delta|^2}. $$

The right-hand-side of (11), (12) is not a usual number but a matrix.

If all the off-diagonal elements between the positive and negative frequencies are zero (i.e., $\delta = \xi = 0$) or negligibly small, the basic equation stands for [17]

$$(\varepsilon_c^{QP} - \varepsilon_v^{QP})A_{vc} + \sum_{v'}\{2X_{vc}A_{vc} \delta_{M,0} - W_{vc}A_{vc} \delta_{M,0}(\Omega)\}A_{vc'} = \Omega A_{vc}.$$ 

In (13), the exchange term $X$ exists only for singlet exciton, having spin multiplicity $M = 0$. Moreover, if only one diagonal element between $v = v' = \text{HOMO}$ and $c = c' = \text{LUMO}$ dominates the others, the magnitude of the
singlet-triplet splitting in the optical absorption peaks amounts to $2X_{\text{exc}}$, which is a well known result.

In the following calculation of Be, a rhombohedral fcc supercell is used with a cubic edge of 30 a.u.. As a basis functions, 5065 PW’s corresponding 12.5 Ry cutoff energy as well as 1s, 2s and 2p AO’s are used. In the evaluation of matrix elements, 5065 $\mathbf{G}(\mathbf{G}^\ast)$ vectors corresponding 12.5 Ry cutoff energy are used for $\Sigma_v(\omega)$ and $(W-U)$, and 40857 $\mathbf{G}$ vectors corresponding 50 Ry cutoff energy are used for $\Sigma_x$ and $U$. In addition, integrations along the radial coordinate are used to evaluate matrix elements of $\Sigma_x$ and $U$ sandwiched by the on-site AO’s only. In the calculation of Mg, Ca and Na$_2$, a slightly larger fcc supercell with a cubic edge of 50 a.u. is employed.

Now I present detailed results of Be, Mg and Ca atoms. Table 1 lists all the terms contributing the GW quasiparticle energies of the HOMO ($s$) state and the LUMO ($p$) states. The columns indicated as ‘exact’ represent the values computed directly with the Herman-Skillman atomic code, which can give exact LDA values for isolated atoms. The experimental value for the HOMO state is the ionization potential with a minus sign. The diagonalization of the full GW matrix is performed in this calculation. Since the correction due to this diagonalization amounts to several tenths of eV, this procedure is quite important. As a result, excellent agreement is obtained between the resulting GW quasiparticle energy and the experimental value.

Table 2 lists the diagonal matrix elements between the HOMO and LUMO states which predominantly contribute to the matrix in the BS equation. Carrying out explicit calculations, I have confirmed that the term $-\mathbf{G}\delta W/\delta \mathbf{G}$ is really negligible. As is seen in this table, the largest term is $U_{\text{exc}}$ which is the direct interaction between particle and hole. The second largest is $X_{\text{exc}}$ which is the exchange interaction appearing only in the singlet exciton. The remaining terms are relatively small compared with these terms. Here it is noted that the off-diagonal elements between positive and negative frequencies contribute a lot to the absorption energies. In particular, in the singlet exciton where the exchange term exists, the off-diagonal elements have a crucial role. And this is really the case for isolated Be, Mg and Ca atoms.

The resulting optical absorption peak energies of isolated Be, Mg and Ca atoms are presented in Table 3. In this table, present results as well as experimental values are listed both for the singlet ($^1S \rightarrow ^1P$) and triplet ($^1S \rightarrow ^3P$) excitons. The resulting optical absorption spectrum of Na$_2$ is shown in Fig.1. Agreement between the present results and the experimental data is good in every case.

In summary, I have carried out the calculation of quasiparticle energies and optical absorption spectra of isolated alkali-earth atoms (Be, Mg and Ca) and small sodium cluster (Na$_2$) by rediagonalizing the full GW matrix and solving
the full BS matrix eigenvalue equation. In the case of Be, Mg and Ca atoms, 
the off-diagonal elements in the $GW$ matrix and also the off-diagonal part 
between positive and negative frequencies in the BS equation play a crucial 
roll in the calculation of the quasiparticle energies and the optical absorption 
spectra.

A part of this work has been done at Physics Department of UC Berkeley 
(UCB). The author is grateful to Prof. Steven G. Louie and the members of 
the Solid State Theory Group at UCB for a lot of helpful discussions and very 
kind hospitality.
References

[1] L. Hedin, New Method for Calculating the One-Particle Green’s Function with Application to the Electron-Gas Problem, Phys. Rev. 139 (1965) A796-A823.

[2] M. S. Hybertsen and S. G. Louie, Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies, Phys. Rev. B 36 (1986) 5390-5413.

[3] R. W. Godby, M. Schlüter and L. J. Sham, Self-energy operators and exchange-correlation potentials in semiconductors, Phys. Rev. B 37 (1988) 10159-10175.

[4] K. Ohno, K. Esfarjani and Y. Kawazoe, Computational Materials Science: From Ab Initio to Monte Carlo Methods, Springer Series on Solid-State Sciences, Vol.129, Springer-Verlag, Berlin, Heidelberg, 1999.

[5] S. Ishii, K. Ohno, Y. Kawazoe and S. G. Louie, Ab initio GW quasiparticle energies of small sodium clusters by an all-electron mixed-basis approach, Phys. Rev. B 63 (2001) 155104;1-6.

[6] S. Ishii, K. Ohno, Y. Kawazoe and S. G. Louie, Ab initio GW quasiparticle calculation of small alkali-metal clusters, Phys. Rev. B 65 (2002) 245109;1-6.

[7] S. Ishii, K. Ohno, V. Kumar and Y. Kawazoe, Breakdown of time-reversal symmetry of photoemission and its inverse in small silicon clusters, Phys. Rev. B 68 (2003) 195412;1-5.

[8] K. Ohno, F. Mauri and S. G. Louie, Magnetic Susceptibility of Semiconductors by an All Electron First-Principle Approach, Phys. Rev. B 56 (1997) 1009-1012.

[9] T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama and K. Masumoto, Insertion of Xe and Kr Atoms in C$_{60}$, C$_{70}$ Fullerenes and Formation of Dimers, Phys. Rev. Lett. 81 (1998) 967-970.

[10] S. Ishii, K. Ohno and Y. Kawazoe, Dielectric Response Functions Studied by an All-Electron Mixed-Basis Approach, Mater. Trans. JIM 40 (1999) 1209-1212.

[11] L. J. Sham and T. M. Rice, Many-Particle Derivation of the Effective-Mass Equation for the Wannier Exciton, Phys. Rev. 144 (1966) 708-714.

[12] G. Onida, L. Reining, R. W. Godby, R. DelSole and W. Andreoni, Ab Initio Calculations of the Quasiparticle and Absorption Spectra of Clusters: The Sodium Tetramer, Phys. Rev. Lett. 75 (1995) 818-821.

[13] M. Rohlfing and S. G. Louie, Excitonic Effects and the Optical Absorption Spectrum of Hydrogenated Si Clusters, Phys. Rev. Lett. 80 (1998) 3320-3323.

[14] M. Rohlfing and S. G. Louie, Optical Excitations in Conjugated Polymers, Phys. Rev. Lett. 82 (1999) 1959-1962.

[15] S. Albrecht, L. Reining, R. D. Sole and G. Onida, Ab Initio Calculation of Excitonic Effects in the Optical Spectra of Semiconductors, Phys. Rev. Lett. 80 (1998) 4510-4513.
[16] G. Strinati, Effects of dynamical screening on resonances at inner-shell thresholds in semiconductors, Phys. Rev. B 29 (1984) 5718-5726.

[17] M. Rohlfing and S. G. Louie, Electron-hole excitations and optical spectra from first principles, Phys. Rev. B 62 (2000) 4927-4944.
Table 1. Contributions to the quasiparticle energies (in eV) for the HOMO and LUMO states are shown compared with the experimental ionization potential and negative of the electron affinity ($-E^{\text{EXP}}$). $\mu^{\text{LDA}}_{\text{x},n} = \langle n | \mu^{\text{LDA}}_{\text{x}} | n \rangle$, $\Sigma_{x,n}$ and $\Sigma_{c,n}$ are Kohn-Sham exchange correlation energy of the LDA, the exchange part, and the correlation part of the self-energy $\Sigma$, respectively.

|     | $\varepsilon_{n}^{\text{LDA}}$ | $\mu_{\text{x},n}^{\text{LDA}}$ | $\Sigma_{x,n}$ | $\Sigma_{c,n}$ | $E^{\text{GWA}}$ | $E^{\text{EXP}}$ |
|-----|-----------------------------|-----------------------------|----------------|----------------|----------------|----------------|
| Be  | 2s                          | -5.61                      | -7.55          | -10.44         | -0.78          | -9.28          | -9.32          |
|     | 'exact'                     | -5.60                      | -7.51          | -10.50         |                |                |                |
|     | 2p                          | -2.11                      | -6.06          | -2.01          | -0.98          | +0.42          | (0.00)         |
|     | 'exact'                     | -2.11                      | -6.07          | -2.08          |                |                |                |
| Mg  | 3s                          | -4.74                      | -7.06          | -9.29          | -0.67          | -7.64          | -7.65          |
|     | 'exact'                     | -4.78                      | -7.06          | -9.36          |                |                |                |
|     | 3p                          | -1.32                      | -4.75          | -1.90          | -0.52          | +1.00          | (0.00)         |
|     | 'exact'                     | -1.39                      | -4.66          | -1.85          |                |                |                |
| Ca  | 4s                          | -3.82                      | -6.03          | -7.56          | -0.63          | -5.98          | -6.11          |
|     | 'exact'                     | -3.85                      | -6.05          | -7.62          |                |                |                |
|     | 4p                          | -1.40                      | -4.29          | -1.76          | -0.50          | +0.63          | (0.00)         |
|     | 'exact'                     | -1.46                      | -4.23          | -1.75          |                |                |                |
Table 2. Explicit values of the BS matrix elements between \( v = \text{HOMO} \) \((s\text{ state})\) and \( c = \text{LUMO} \) \((p\text{ states})\) of Be, Mg and Ca in units of eV. Both the direct term \( W_{vc;vc} = U_{vc;vc} + S_{vc;vc} \) and the exchange term \( X_{vc;vc} \) exist in the diagonal \( 4 \times 4 \) submatrix, while \( -\delta_{vc;vc} = U_{vc;vc} + S_{vc;vc} \) and \( \xi_{vc;vc} = X_{vc;vc} \) exist in the off-diagonal \( 4 \times 4 \) submatrix.

| Atom | \( U_{vc;vc} \) | \( S_{vc;vc} \) | \( X_{vc;vc} \) | \( U_{vc;vc} \) | \( S_{vc;vc} \) | \( X_{vc;vc} \) |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Be   | 8.67            | -0.67           | 1.79            | 0.96            | -0.58           | 1.79            |
| Mg   | 6.45            | -0.60           | 1.32            | 0.80            | -0.77           | 1.32            |
| Ca   | 5.28            | -0.45           | 1.11            | 0.61            | -0.68           | 1.11            |

Table 3. The comparison between singlet and triplet energies (in eV) calculated from the BS equation. The experimental values are also listed for comparison.

| Atom | Transition \( 1S \to \) \( ^1P \) | Present result | Experiment |
|------|---------------------------------|----------------|------------|
| Be   | \( ^1S \to ^3P \)              | 5.4            | 5.28       |
| Mg   | \( ^1S \to ^3P \)              | 2.6            | 2.72       |
| Ca   | \( ^1S \to ^1P \)              | 4.6            | 4.34       |
|      | \( ^1S \to ^3P \)              | 2.4            | 2.72       |