Double ionization energy spectra of small alkali-metal clusters

Yoshifumi Noguchia, Soh Ishiia,b, Yoshiyuki Kawazoeb, Kaoru Ohnoa,*

a Department of Physics, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
b Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8501, Japan

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Abstract

In this article, we calculate the spectra of the double ionization energy (the energy required for adding two electrons to the neutral system) of small alkali-metal clusters (K$_2$ and Li$_2$) including the effect of electron–electron short-range correlation by adding two one-particle energies within the GW approximation and taking into account the electron–electron repulsive interaction effectively.

Keywords: First principles; Ladder diagram; Bethe–Salpeter equation; T-matrix theory; All-electron mixed basis approach

1. Introduction

The problem of electron correlations is particularly important for small clusters because of the confined geometry. So far, the single ionization (quasiparticle) energy spectra of small alkali-metal clusters have been calculated with the state-of-the-art GW approximation (GWA) [1], using the all-electron mixed basis approach [2–4], in which each wave function is expanded in linear combination of both atomic orbitals (AO’s) and plane waves (PW’s). The GWA is based on the time-dependent many-body perturbation theory, and can be constructed from the Hartree-Fock approximation by replacing the bare Coulomb interaction in the Fock exchange term with the dynamically screened Coulomb interaction $W$ evaluated within the random phase approximation (RPA) [5].

In the present study, we focus on the double ionization energy spectra, which are interpreted as the energy required for adding two electrons to the neutral system. In contrast to the single ionization energy, the double ionization energy strongly reflects the electron–electron repulsive interaction. Therefore, they are generally not given by the simple addition of two one-particle energies which may be obtained within the GWA. Here, we take into account the electron–electron repulsive interaction effectively to calculate the double ionization energy spectra of Li$_2$ and K$_2$ clusters.

2. Methodology

Throughout this article, we expand wave functions by using all-electron mixed basis approach [1–4], in which localized part around nucleus is represented by AO’s and extended part all over the unit cell is represented by PW’s. All core and valence AO’s are generated by Herman-Skillman’s atomic code [6] within the non-overlapping atomic spheres. We start from the local density approximation (LDA) within the density functional theory. Then we go on to the GWA and its correction.

2.1. GW approximation

Quasiparticle energy is obtained by solving the Dyson’s equation

\[ (H_0 + V_H - E_p)\psi_p(r_1) + \int \bar{r}' \sum (r_1, r_1'; E_e) \psi_p(r_1') = 0. \]  

(1)
We introduce the following components in short-hand notation \( \equiv (r,t) \)

\[
W(1,1')^+ = U(1,1') + \int d2d3U(1,2)P(2,3)W(3,1'),
\]

\[
P(1,1'), = -iG(1,1'^+)G(1',1),
\]

where \( G \) is the one particle Green’s function, \( U \) is the bare Coulomb interaction, \( W \) is the dynamically screened Coulomb interaction and \( P \) is the polarizability function within the random phase approximation (RPA) [5]. In Eq. (4), \( 1^+ \) means that \( t \rightarrow t + \delta \) where \( \delta \) is a positive infinitesimal. Then electron self-energy is given by

\[
\sum_{\text{GWA}} (1,1') = iG(1,1')W(1,1')
\]

within the GWA. We use the LDA wave functions and the LDA eigenvalues to evaluate \( G \) and \( W \) from the viewpoint of perturbation theory. In the calculation, we employ an fcc supercell with a cubic edge of 50 a.u. and use 2975 PW’s corresponding 3.1 Ry cutoff energy. We use also 2975 \( \mathbf{G}(\mathbf{G}') \) vectors corresponding 3.1 Ry cutoff energy for \( \Sigma_c(w) \) and \( (W-U) \), and 23589 \( \mathbf{G} \) vectors corresponding 12.5 Ry cutoff energy for \( \Sigma_c \) and \( U \). The other detail of the calculation in the GWA is already given in Ref. [1].

If we neglect the interaction between the two additional electrons, the double ionization energy spectra become just the simple addition of the two one-particle energies obtained within the GWA.

2.2. Electron–electron repulsive interaction

In order to take into account the effect of the electron–electron correlation in our calculation, it is in principle possible to introduce the \( T \)-matrix theory that describes multiple scattering between two electrons. The \( T \)-matrix satisfies the following Bethe–Salpeter equation [7]

\[
T(1,2|3,4) = W(1,2)\delta(1-3)\delta(2-4)
+ iW(1,2)\int d1'd2'K(1,2|1',2')T(1',2'|3,4),
\]

where \( K \) is two-particle propagator

\[
K(1,2|1',2') = iG(1',1)G(2',2).
\]

Here we put \( W(1,2) = W(r_1,r_2)\delta(t_1-t_2) \) in the static approximation. Diagrammatically, this equation is shown in Fig. 1. The Bethe–Salpeter equation (5) can be rewritten by introducing matrix elements sandwiched by the LDA wave functions. Then the original equation is converted to an eigenvalue problem. Then the spectra of the eigenvalues give directly the double ionization spectra.

Because this is still a bit too demanding problem, here we use the following alternative approach. We consider only several matrix elements between low lying empty levels and evaluate the deviation from the simple addition of the two GWA quasiparticle energies perturbatively.

3. Results

Fig 2(a) and (b) (dotted lines) show the results of the double ionization energy spectra obtained by the simple addition of the two GWA quasiparticle energies for \( \text{K}_2 \) and \( \text{Li}_2 \) clusters, respectively. In these figures, the energy zero means the vacuum level. Note that the calculated spectra are those constructed only by the combination of 25 single
particle levels. Therefore the resulting spectra in high energy side are artificially truncated.

We notice that there are several peaks in the region of negative energies within the GWA, which might suggest the existence of the bound state. However, this is a wrong result because K₂⁻ and Li₂⁻ are experimentally unstable. In order to improve this GWA result, we estimated the correction due to the electron-electron repulsive interaction approximately as 2 eV for K₂ and 1.5 eV for Li₂. Then the spectra are constantly shifted to the higher energy side by these amounts. The resulting spectra are depicted by solid lines in Fig. 2(a) and (b). Obviously the bound state no longer exists in this corrected curves, which indicate that K₂⁻ and Li₂⁻ are really unstable.

4. Summary

In this article, we have estimated the double ionization energy spectra of lithium and potassium dimers first by simply adding two one-particle energies obtained within the GWA and then by shifting the spectra by a constant amount which is estimated from an approximate calculation on the basis of the T-matrix theory. The corrected curves predicts that no bound state exists for K₂⁻ and Li₂⁻.

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