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## Quasiparticle energies in small alkali-metal clusters

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**Abstract.** We have calculated the quasiparticle energies of sodium and potassium clusters using the jellium-sphere-background model for the positive ion cores. The electron self-energy is evaluated in first order in the screened Coulomb interaction with local field effects included. Results show significant improvements over the Kohn–Sham eigenvalues in the local-density-functional theory both for the occupied and for the unoccupied quasiparticle states. The theory is found to give the correct size dependencies for quasiparticle energies in the finite systems.

### 1. Introduction

Since the experimental mass spectra for sodium clusters were found to be explained by the shell structures of valence electrons [1], many theoretical and experimental studies on metal clusters have been done. The results confirmed the existence of electronic shell structures in the simple-metal clusters [2]. The experimental ionization potentials [3] and static polarizabilities [4] as well as the mass spectra for alkali-metal clusters show discontinuities at the shell-closing cluster size obtained theoretically using the jellium-sphere-background model [1, 5–7] and the Hohenberg–Kohn–Sham local-density-functional approximation (LDA) [8, 9].

In the jellium-sphere-background model, the positive ion cores in the cluster are replaced by a sphere with constant density, which is usually set equal to the bulk valence-electron density. Then, the radius of the sphere for an  $n$ -atom cluster is  $r_s n^{1/3}$ , where  $r_s$  is the Wigner–Seitz radius. Interacting valence electrons bound in the potential of the jellium sphere are usually treated in the LDA. The calculated closed-shell cluster sizes for alkali-metal clusters are  $n = 2, 8, 18, 20, 34, 40$ , and so on, corresponding to  $1s, 1p, 1d, 2s, 1f$  and  $2p$  shell-closing structures.

In a wide variety of electronic-structure calculations, the LDA eigenvalues, that is the eigenvalues of the self-consistent Kohn–Sham equations with the local exchange–correlation potential, have often been used to estimate the one-particle energies of the interacting electrons (quasiparticle energies). There are, however, considerable differences between the LDA eigenvalues and the experimental quasiparticle energies both in finite and infinite systems. In the case of infinite bulk semiconductors, for

instance, the LDA usually gives band gaps which are too small and, as an extreme case, for example, gives a metallic electronic structure for germanium. It has been pointed out that not only the LDA but also the 'true' exchange–correlation potential, although not known, will give smaller band gaps if the Kohn–Sham eigenvalues are used for the quasiparticle energies [10,11]. In the LDA calculation for atoms, the highest-occupied states are too shallow to give an accurate estimate of the measured first ionization potentials. The LDA lowest-unoccupied states are, on the other hand, too deep to give the correct electron affinities of atoms. The LDA eigenvalues for alkali-metal clusters have similar problems. Although the LDA occupied-state sequences in the jellium-sphere-background model for sodium and potassium clusters are almost the same and show good accordance with experimental shell structures, the occupied states are too shallow and the unoccupied states are too deep as in the case of atoms. Therefore, this problem is not expected to arise from the jellium-sphere-background model but from the LDA.

Recently, for the infinite systems, the Hybertsen–Louie approach [12], which is based on the Hedin GW approximation [13,14] and includes local-field effects, has been shown to give much better quasiparticle energies than the LDA. In the GW approximation, the self-energy operator is given by the product of the electron Green function  $G$  and the screened Coulomb interaction  $W$ . The Hybertsen–Louie-type calculations have been applied not only to semiconductors [12,15–19] but also to metals [20,21], and it gives better accord with experiments than the LDA. Furthermore, the GW quasiparticle theory has been found to work at surfaces and interfaces [22,23].

In the present work, we have extended the quasiparticle approach to the closed-shell sodium and potassium clusters in the jellium-sphere-background model. (A brief report of some of the cluster results has been published [24].) To our knowledge, this is the first application of the GW approximation to finite systems. The GW approximation in the finite systems is also expected to give much better quasiparticle energies than the LDA. In section 2 the general formalism of the GW quasiparticle approximation for spherical systems including a new approximate method to give the screened Coulomb interaction  $W$  will be reviewed. Results will be given and compared to the experimental quasiparticle energies (ionization thresholds and electron affinities) in section 3. The relationship between the present quasiparticle theory and other theories will be discussed in section 4. A brief summary and conclusion will be given in section 5.

## 2. Formalism

### 2.1. Quasiparticle energies in the GW approximation

Even in the interacting many-particle systems, one-particle excitations are often well-defined states with long lifetimes and are identified as the quasiparticle states. The valence electrons in simple-metal clusters are expected to have well-defined one-electron states corresponding to the experimentally observed electronic shell structures. These quasiparticle states satisfy the following equation [12,13]:

$$H^H(\mathbf{r})\phi_i(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_i)\phi_i(\mathbf{r}') = E_i\phi_i(\mathbf{r}) \quad (1)$$

where  $H^H(\mathbf{r})$  is the Hartree Hamiltonian consisting of the kinetic energy operator, the external potential, and the Hartree potential based on the total electron density.  $\phi_i(\mathbf{r})$

and  $E_i$  are the quasiparticle wavefunction and the quasiparticle energy, respectively.  $\Sigma(\mathbf{r}, \mathbf{r}'; E)$  is the energy-dependent non-local self-energy operator. Since the self-energy operator is non-Hermitian, the quasiparticle energy  $E_i$  is generally complex and the quasiparticle state has a finite lifetime. The  $\text{Im}E_i$  is positive and negative for occupied and unoccupied states, respectively.

In the GW approximation,  $\Sigma$  is given by the first-order term in a perturbation series with respect to the screened Coulomb interaction  $W$ . This corresponds to considering the zeroth-order term for the vertex function [13, 14]. Then, for non-magnetic systems, the self-consistent equations to be solved are

$$\Pi(\mathbf{r}_1, \mathbf{r}_2; E) = 2 \int_{-\infty}^{\infty} \frac{dz}{2\pi i} G(\mathbf{r}_1, \mathbf{r}_2; E) G(\mathbf{r}_2, \mathbf{r}_1; z - E) \quad (2)$$

$$W(\mathbf{r}_1, \mathbf{r}_2; E) = v(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 \int d\mathbf{r}_4 v(\mathbf{r}_1, \mathbf{r}_3) \Pi(\mathbf{r}_3, \mathbf{r}_4; E) W(\mathbf{r}_4, \mathbf{r}_2; E) \quad (3)$$

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2; E) = \int_{-\infty}^{\infty} \frac{dz}{2\pi i} e^{-i\eta z} G(\mathbf{r}_1, \mathbf{r}_2; E - z) W(\mathbf{r}_1, \mathbf{r}_2; z) \quad (4)$$

$$[E - H^H(\mathbf{r}_1)]G(\mathbf{r}_1, \mathbf{r}_2; E) - \int d\mathbf{r}_3 \Sigma(\mathbf{r}_1, \mathbf{r}_3; E) G(\mathbf{r}_3, \mathbf{r}_2; E) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (5)$$

in energy space. Here,  $\Pi$  is the irreducible polarization propagator after the spin sum,  $v$  is the bare Coulomb interaction, and  $\eta$  is a positive infinitesimal.

Within the quasiparticle approximation, the electron Green function is written as

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_i \frac{\phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}')}{E - E_i} \quad (6)$$

which, together with (5), gives the quasiparticle equation (1). If we use the time-ordered density-density response function  $\chi$ , we can rewrite equation (3) for  $W$  in a closed form

$$W(\mathbf{r}_1, \mathbf{r}_2; E) = v(\mathbf{r}_1, \mathbf{r}_2) + \int d\mathbf{r}_3 \int d\mathbf{r}_4 v(\mathbf{r}_1, \mathbf{r}_3) \chi(\mathbf{r}_3, \mathbf{r}_4; E) v(\mathbf{r}_4, \mathbf{r}_2). \quad (7)$$

For a non-magnetic system,  $\chi$  is generally given as

$$\chi(\mathbf{r}, \mathbf{r}'; E) = \sum_m N_m(\mathbf{r}) \left( \frac{1}{E - \omega_m + i\eta} - \frac{1}{E + \omega_m - i\eta} \right) N_m(\mathbf{r}') \quad (8)$$

where  $\omega_m$  is the (exact) excitation energy of the  $m$ th excited state  $|m\rangle$  from the ground state  $|0\rangle$ , and

$$N_m(\mathbf{r}) = \langle 0 | \hat{n}(\mathbf{r}) | m \rangle = \langle m | \hat{n}(\mathbf{r}) | 0 \rangle. \quad (9)$$

Here,  $\hat{n}(\mathbf{r})$  is the electron-density operator. Equations (6)–(8) give the useful expression for the self-energy operator through a contour integral on the lower half plane

$$\begin{aligned} \Sigma(\mathbf{r}_1, \mathbf{r}_2; E) = & - \sum_i^{\text{occ}} \phi_i(\mathbf{r}_1) \phi_i^*(\mathbf{r}_2) W(\mathbf{r}_1, \mathbf{r}_2; E - E_i) \\ & + \sum_m V_m(\mathbf{r}_1) V_m(\mathbf{r}_2) G(\mathbf{r}_1, \mathbf{r}_2; E - \omega_m) \end{aligned} \quad (10)$$

where

$$V_m(\mathbf{r}) = \int d\mathbf{r}' v(\mathbf{r}, \mathbf{r}') N_m(\mathbf{r}'). \quad (11)$$

Although only the zeroth-order vertex function is used in the GW approximation, the self-consistent equations (2)–(5) are still very complicated for real systems. If we can calculate  $W$  (or  $\chi$ ) and  $G$  separately, the quasiparticle energies can be evaluated using (1) and (10). To take advantage of this approach, the Green function from the LDA will be used for the electron Green function, and  $\chi$  will also be given using the time-dependent local-density approximation (TDLDA) [26, 27].

### 2.2. Green function in the LDA

For spherical systems, the Green function can be expanded using Legendre functions  $P_l$

$$G(\mathbf{r}_1, \mathbf{r}_2; E) = \sum_l \frac{2l+1}{4\pi} P_l(\cos\theta) G_l(r_1, r_2; E) \quad (12)$$

where  $\theta$  is the angle between  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . Then, within the LDA,  $G_l$  is given by [26, 27]

$$G_l(r_1, r_2; E) = \frac{j_l(r_{<}; E) h_l(r_{>}; E)}{r^2 [j_l(r; E) h_l'(r; E) - j_l'(r; E) h_l(r; E)]} \quad (13)$$

where  $r_{<} = \min(r_1, r_2)$  and  $r_{>} = \max(r_1, r_2)$ , and the denominator is the Wronskian independent of  $r$ .  $j_l$  and  $h_l$  are the solutions of the boundary-value problem of the Schrödinger equation with the LDA effective potential. We calculate the retarded Green function  $G_l^R$  by (13) with the boundary conditions that  $j_l$  is to be regular as  $r \rightarrow 0$  and that  $h_l$  is to be an outgoing wave as  $r \rightarrow \infty$ . If necessary,  $G^R$  can be converted to its time-ordered function  $G$  by

$$G(\mathbf{r}, \mathbf{r}'; E) = \begin{cases} G^R(\mathbf{r}, \mathbf{r}'; E) & (E > \mu) \\ G^{R*}(\mathbf{r}', \mathbf{r}; E) & (E \leq \mu) \end{cases} \quad (14)$$

where  $\mu$  is the highest-occupied-state energy in the LDA.

### 2.3. TDLDA density–density response function

Usually, in the TDLDA, the retarded density–density response function  $\chi^R$  is considered [26, 27]. ( $\chi = \chi^R$  for  $E \geq 0$  and  $\chi = \chi^{R*}$  for  $E < 0$ .) The TDLDA  $\chi^R$  is given by

$$\chi^R(\mathbf{r}_1, \mathbf{r}_2; E) = \chi^0(\mathbf{r}_1, \mathbf{r}_2; E) + \int d\mathbf{r}_3 \int d\mathbf{r}_4 \chi^0(\mathbf{r}_1, \mathbf{r}_3; E) K(\mathbf{r}_3, \mathbf{r}_4) \chi^R(\mathbf{r}_4, \mathbf{r}_2; E) \quad (15)$$

where  $\chi^0$  is the (retarded) Kohn–Sham independent-particle density–density response function and the kernel  $K$  is given as

$$K(\mathbf{r}, \mathbf{r}') = v(\mathbf{r}, \mathbf{r}') + \frac{dV_{xc}}{d\rho} \delta(\mathbf{r} - \mathbf{r}'). \quad (16)$$

Here,  $\rho$  is the electron density and  $V_{xc}$  is the (local) exchange–correlation potential. In the present work, Wigner’s interpolation formula [28] is used for the correlation energy. Equation (15) has been derived from the self-consistent effective-field concept as in the case of the random-phase approximation (RPA). In the TDLDA, however, the interaction between electrons is considered to be  $K(\mathbf{r}, \mathbf{r}')$  rather than  $v(\mathbf{r}, \mathbf{r}')$  in the RPA. Therefore, the TDLDA is expected to include the vertex correction to some extent.

The TDLDA  $\chi^0$  is given as

$$\chi^0(\mathbf{r}_1, \mathbf{r}_2; E) = 2 \sum_i^{\text{occ}} [\psi_i(\mathbf{r}_2) \psi_i^*(\mathbf{r}_1) G^{\text{R}}(\mathbf{r}_1, \mathbf{r}_2; \epsilon_i + E) + \psi_i(\mathbf{r}_1) \psi_i^*(\mathbf{r}_2) G^{\text{R}*}(\mathbf{r}_1, \mathbf{r}_2; \epsilon_i - E)] \quad (17)$$

where  $\epsilon_i$  and  $\psi_i$  are the eigenvalues and the eigenfunctions of the LDA Kohn–Sham equation, respectively.  $G^{\text{R}}$  is the retarded LDA Green function. Equations (15)–(17) enable us to calculate  $\chi(\mathbf{r}, \mathbf{r}'; E)$  for a given energy  $E$ . It is, however, still not straightforward to calculate the excitation spectrum  $\omega_m$  and  $N_m$  (or  $V_m$ ), which are necessary in order to evaluate the self-energy operator  $\Sigma$  from (10).

In the present work, we use a new formalism to calculate  $\omega_m$  and  $N_m$  from the (TDLDA) temperature density–density response function  $\chi^T(\mathbf{r}_1, \mathbf{r}_2; iy)$  (as the temperature  $T \rightarrow 0$ ). The method has been presented previously [24] and will be discussed in more detail elsewhere [29].  $\chi^T(\mathbf{r}_1, \mathbf{r}_2; iy)$  with positive  $y$  is the analytic continuation of  $\chi^{\text{R}}(\mathbf{r}_1, \mathbf{r}_2; E)$ . Therefore, the TDLDA  $\chi^T$  can be calculated in the same way as the TDLDA  $\chi^{\text{R}}$ . The basic assumption used in the new formalism is that the matrix  $\mathbf{N}$  ( $[\mathbf{N}]_{m\mathbf{r}} = N_m(\mathbf{r})$ ) is square (square-matrix approximation). Then, the  $\chi^T(\mathbf{r}_1, \mathbf{r}_2; iy)$  at two different points  $y = y_1$  and  $y_2$  are necessary and sufficient to determine  $\omega_m$  and  $N_m(\mathbf{r})$ .

Since the density-functional theory, in principle, gives us the exact static ground-state properties, the LDA  $\chi(\mathbf{r}_1, \mathbf{r}_2; 0)$  is expected to be fairly accurate. We therefore use very small  $y_1$  (0.01 Ryd). ( $y_1=0$  cannot be used in the present TDLDA procedure since both the first and the second term in (17) diverge for zero energy, although they, in principle, must cancel each other to give the finite value for the static  $\chi^0$ .) On the other hand,  $y_2$  should be comparable to the important excitation energies, that is  $\omega_m$  with large oscillator strengths (cf. equation (16) in [24]). Such important excitations are, in general, the collective modes. In the case of metal clusters, the collective modes are expected to be the surface plasma resonances and to have energies comparable to (but less than) the bulk plasmon energy [30–33]. The bulk plasmon energies for potassium and sodium are 0.3 ~ 0.4 Ryd. Therefore,  $y_2 = 0.5$  Ryd will be used here. Using these  $y_1$  and  $y_2$  values, the square-matrix approximation is found to give energies and strengths of collective excitations quantitatively very well. Moreover, the  $y_1$  and  $y_2$  dependences of the collective excitations are found to be very weak [29]. Since the collective excitations have dominant strengths in the excitation spectra, the results of the present paper also have very weak  $y_1$  and  $y_2$  dependences. Another set of  $y_1$  and  $y_2$  values,  $y_1=0.05$  and  $y_2=0.3$  (Ryd), for example, gives quasiparticle energies almost identical to those given in the present paper. (The maximum difference is less than 0.1 eV.)

#### 2.4. Quasiparticle wavefunction

In the GW quasiparticle calculations for bulk semiconductors, it has been found that the LDA wavefunctions approximate the corresponding quasiparticle wavefunctions

very well [12]. Therefore, we use the LDA  $\psi_i$  for the quasiparticle wavefunctions  $\phi_i$ . Then, we can evaluate the quasiparticle energies as

$$E_i = \epsilon_i - \int d\mathbf{r} \psi_i^*(\mathbf{r}) V_{xc} \psi_i(\mathbf{r}) + \int d\mathbf{r} \int d\mathbf{r}' \psi_i^*(\mathbf{r}) \Sigma(\mathbf{r}, \mathbf{r}'; E_i) \psi_i(\mathbf{r}'). \quad (18)$$

In the present work,  $E_i$  is assumed to be real.

Since the similarity between the LDA wavefunctions and the GW quasiparticle wavefunctions in finite systems may be different from that of the bulk infinite case, we have estimated the difference between the LDA  $\psi_i$  and the GW  $\phi_i$  in the following way. Using matrix notation, the quasiparticle equation is written as

$$[\mathbf{H}^H + \Sigma(E_i)]\phi_i = E_i\phi_i. \quad (19)$$

To estimate  $\phi_i$  by (19), we have used  $\Sigma(E_i)$  given by (10) and (18). Then,  $\phi_i$  is given as the eigenvector of the matrix  $\mathbf{H}^H + \Sigma(E_i)$ . We have confirmed that  $\phi_i$  calculated in this way is very close to  $\psi_i$ . In most cases, the overlap  $S_i = \langle \phi_i | \psi_i \rangle$  is 0.99 or even closer to unity. In some exceptional cases,  $S_i$  is less than 0.99 ( $S_{1p}(\text{Na}_2)=0.98$ ,  $S_{1s}(\text{Na}_{34})=0.97$ , and  $S_{1s}(\text{K}_{34})=0.96$ ). Although the origin of these exceptions is not clear,  $\phi_i$  and  $\psi_i$  are still close to each other. Moreover, even in such cases,  $E_i$  evaluated using  $\psi_i$  is expected to be very close to that using  $\phi_i$ , since the quasiparticle energy is a stationary value as a functional of the quasiparticle wavefunction and has a higher-order accuracy than the wavefunctions.

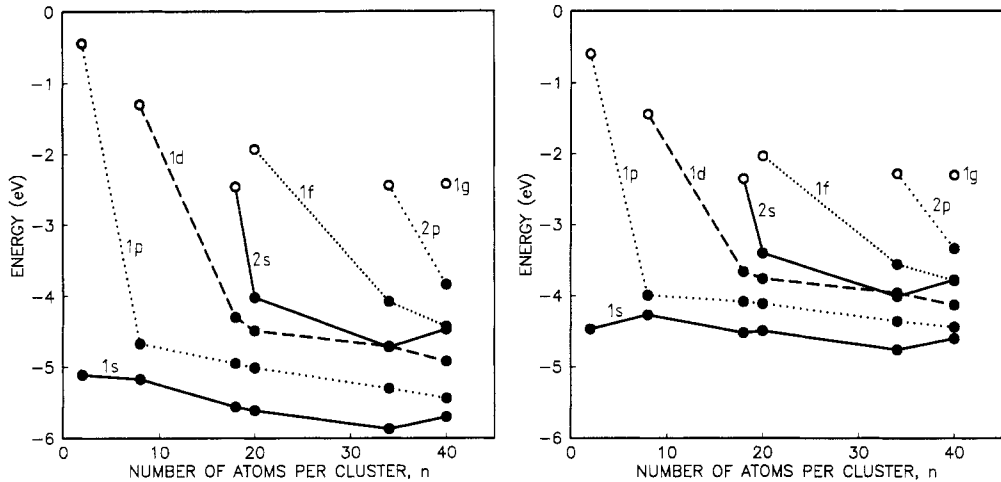
Since the systems considered have spherical symmetry, we can use the expansion in Legendre functions for physical values similar to the electron Green function in section 2.2. Several equations in this section are rewritten for spherical systems and are given in the appendix.

### 3. Results

#### 3.1. Quasiparticle energies

In the present work,  $r_s = 4$  and 4.86 (a.u.) are used for  $\text{Na}_n$  and  $\text{K}_n$  respectively. In figure 1, the calculated quasiparticle energies for the closed-shell  $\text{Na}_n$  and  $\text{K}_n$  ( $n = 2, 8, 18, 20, 34$ , and 40) are given. Within the GW approximation, the electronic shell structure sequences are almost the same as in the LDA. A change in the sequences is found only in the case of  $n = 34$  (both for Na and K):  $\epsilon_{1d} < \epsilon_{2s}$  while  $E_{1d} > E_{2s}$ . However, the absolute values of the GW  $E_i$  are considerably different from the LDA  $\epsilon_i$ . In table 1, the LDA  $\epsilon_i$  and the GW  $E_i$  are listed together with the self-interaction corrected LDA (SIC) results. The SIC is known to give much better occupied one-particle energies for atoms than the LDA [34, 35], although the foundation for such an approach remains to be justified. The SIC results for the  $\text{Na}_n$  and  $\text{K}_n$  in the jellium-sphere-background model are improved compared to the LDA. The SIC one-particle states are deeper than in the LDA and the highest-occupied-state  $\epsilon_i$  give much better ionization potentials [36]. The occupied GW quasiparticle states are also found to be considerably deeper than in the LDA and are expected to be much better than in the LDA. The photoelectron spectra for  $\text{Na}_n$  and  $\text{K}_n$  will give the occupied  $E_i$  to be compared to the present calculation.

On the other hand, the unoccupied GW quasiparticle  $E_{1g}$  for  $\text{K}_{40}$  is shallower than the LDA  $\epsilon_{1g}$ . Therefore, the many-body correction to the LDA  $\epsilon_i$  has different signs



**Figure 1.** Calculated occupied (full circles) and unoccupied (open circles) quasiparticle energies of the closed-shell alkali-metal clusters:  $\text{Na}_n$  (left-hand figure) and  $\text{K}_n$  (right-hand figure) ( $n = 2, 8, 18, 20, 34$  and  $40$ ).

**Table 1.** Occupied-state (1s to 2p) and unoccupied-state (1g) quasiparticle energies for  $\text{K}_{40}$  in the jellium-sphere-background model obtained using the LDA, SIC and the current GW approximation (eV). The LDA and SIC results are also our own values.

$i$	LDA $\epsilon_i$	SIC $\epsilon_i$	GW $E_i$
1s	-4.3	-4.8	-4.6
1p	-4.1	-4.5	-4.4
1d	-3.6	-4.0	-4.1
2s	-3.2	-3.7	-3.8
1f	-3.1	-3.4	-3.8
2p	-2.5	-3.0	-3.3
1g	-2.5	-2.8	-2.3

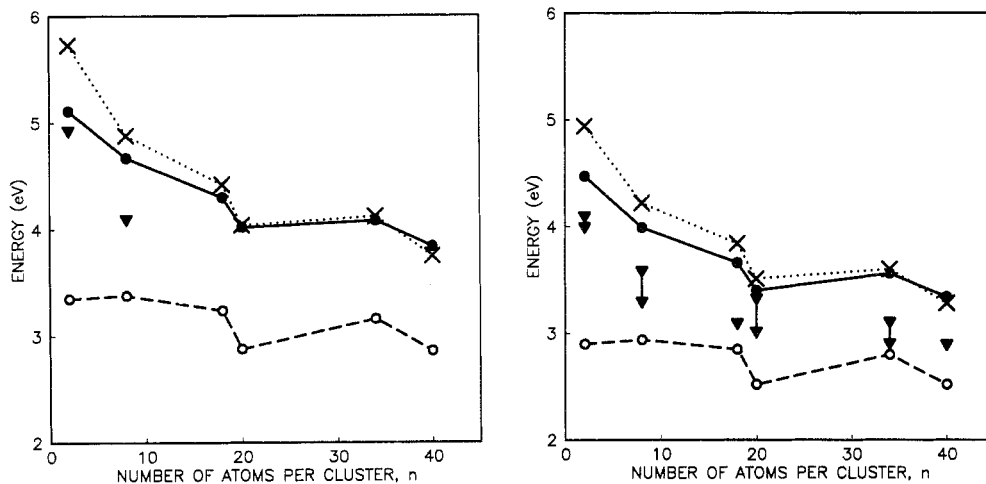
for the occupied and the unoccupied states, respectively. The bulk semiconductor quasiparticle energies also have the same properties [12]. The SIC is expected to work only for the occupied states because the original motivation is to remove the Hartree and exchange–correlation contributions coming from the electron itself from the LDA effective potential for each electron. Actually, the SIC unoccupied-state energy  $\epsilon_{1g}$  for  $\text{K}_{40}$  is even deeper than the LDA  $\epsilon_{1g}$  which is already too deep.

### 3.2. Ionization potentials

Since the quasiparticle energies are defined as the energy changes when one electron is added or removed from the system, the absolute values of the highest-occupied-state energies ( $E_{\text{HO}}$ ) correspond to the first ionization potentials. In figure 2,  $|E_{\text{HO}}|$  for  $\text{Na}_n$  and  $\text{K}_n$  are compared with the LDA  $|\epsilon_{\text{HO}}|$ , to the ionization potentials calculated as the LDA total-energy difference between the  $\text{Na}_n^+$  ( $\text{K}_n^+$ ) and the  $\text{Na}_n$  ( $\text{K}_n$ ), and to the experimental photoionization thresholds [2, 37–39]. In both  $\text{Na}_n$  and  $\text{K}_n$ , the GW  $|E_{\text{HO}}|$  are found to be much larger than the LDA  $|\epsilon_{\text{HO}}|$  and follow the total-energy differences very closely. The LDA total-energy difference is expected to give rather



accurate ionization potentials for jellium spheres as in the case of atoms. Therefore, the GW  $E_{\text{HO}}$  is expected to be very close to the ideal values for the jellium spheres.



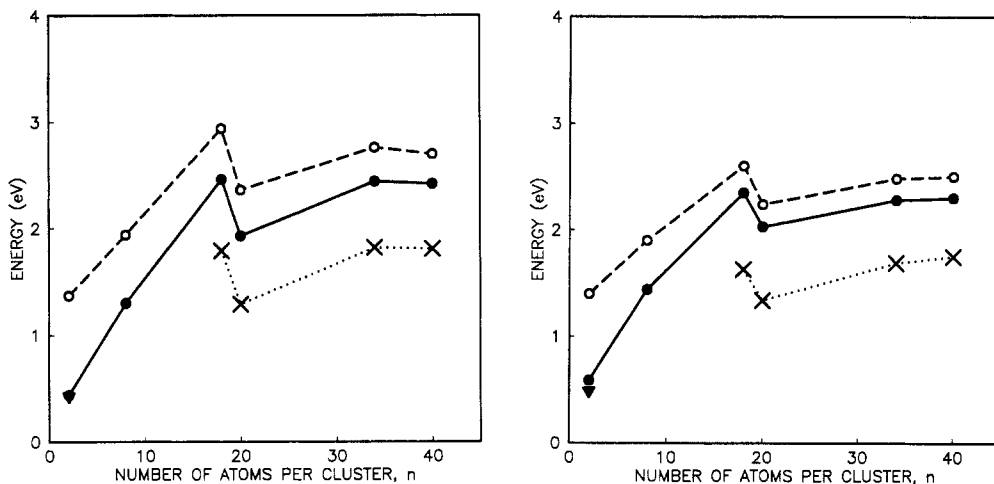
**Figure 2.** The absolute values of the quasiparticle energies of the highest-occupied states in sodium (left-hand figure) and potassium (right-hand figure) clusters obtained using the LDA (open circles) and the GW approximation (full circles). The crosses represent the LDA total-energy differences between the positive ( $\text{Na}_n^+$  and  $\text{K}_n^+$ ) and the neutral clusters ( $\text{Na}_n$  and  $\text{K}_n$ ). The experimental ionization thresholds are given by the triangles (data from [2, 37–39]).

The GW  $|E_{\text{HO}}|$  is found to have much stronger size dependence than the LDA  $|\epsilon_{\text{HO}}|$ . The smaller clusters have larger  $|E_{\text{HO}}|$  in accord with the size dependence of the experimental photoionization thresholds. The experimental ionization thresholds are, in general, smaller than the GW  $|E_{\text{HO}}|$ . In the case of real clusters, the non-spherical potential from the ion cores will lift the degeneracy of the highest-occupied states and will give a new position for the highest-occupied state, which will be shallower than the original one in the case of closed-shell clusters. Therefore, the remaining discrepancy between the GW  $|E_{\text{HO}}|$  and the experimental photoionization thresholds probably arises from the jellium-sphere-background model. (It may also come from the finite-temperature effect in the experiment. The hotter clusters are believed to have lower ionization thresholds [2, 39].)

### 3.3. Electron affinities

The absolute values of the lowest-unoccupied quasiparticle energies,  $|E_{\text{LU}}|$  correspond to the the electron affinities of the clusters. In figure 3, the GW  $|E_{\text{LU}}|$  and the LDA  $|\epsilon_{\text{LU}}|$  are given. The LDA total-energy differences between the  $\text{Na}_n$  ( $\text{K}_n$ ) and the  $\text{Na}_n^-$  ( $\text{K}_n^-$ ) are also given in figure 3. For smaller negative clusters ( $n = 2$  and  $8$ ), however, the LDA calculation is impossible since the highest-occupied states become extended states.

As in the case of  $\text{K}_{40}$ , the GW  $|E_{\text{LU}}|$  are always smaller than the LDA  $|\epsilon_{\text{LU}}|$  and are closer to the total-energy differences. As for the experimental electron affinities of  $\text{Na}_n$  and  $\text{K}_n$ , only a few results are available. The recent photoelectron spectra of  $\text{Na}_2^-$  and  $\text{K}_2^-$  have given  $0.430 \pm 0.015$  and  $0.493 \pm 0.012$  (eV) as the electron affinities of  $\text{Na}_2$  and  $\text{K}_2$ , respectively, in good accord with the present GW  $E_{1p}$ .



**Figure 3.** The absolute values of the quasiparticle energies of the lowest-unoccupied states in sodium (left-hand figure) and potassium (right-hand figure) clusters obtained using the LDA (open circles) and the GW approximation (full circles). The LDA total-energy differences between the neutral ( $\text{Na}_n$  and  $\text{K}_n$ ) and the negative clusters ( $\text{Na}_n^-$  and  $\text{K}_n^-$ ) are given by the crosses. The LDA calculation is not possible for smaller negative clusters ( $n = 2$  and  $8$ ). The experimental electron affinities for  $\text{Na}_2$  and  $\text{K}_2$  are given by the triangles (data from [40]).

#### 4. Discussion

The present work has verified that the LDA wavefunctions in finite systems as well as in infinite systems are very good quasiparticle wavefunctions, even though the LDA Kohn-Sham eigenvalues are rather poor approximations for quasiparticle energies. This result is consistent with the fact that the SIC works in finite systems in spite of the fact that its basic assumption is not well-founded. In the SIC formalism, the Kohn-Sham eigenfunctions are treated as if they are the one-particle (quasiparticle) wavefunctions in the interacting many-electron systems, even though they are the wavefunctions of hypothetical non-interacting systems. (The LDA and the SIC wavefunctions are very close to each other in the finite systems.)

Once we regard the LDA wavefunctions as quasiparticle wavefunctions, the Hartree potential for each particle in the Kohn-Sham equations involves the Coulomb potential from the particle itself. In the Hartree-Fock approximation (HF), this self-Coulomb-potential term is cancelled out by the counter term in the exchange potential, while the cancellation is not complete in the LDA formalism. The self-interaction problem in the LDA is more serious in smaller systems, and conceals the strong size dependence of the highest-occupied-state energies. The present quasiparticle calculation for alkali-metal clusters has revealed the generality and the usefulness of the GW approximation even for the finite systems. The calculated quasiparticle energies give the correct size dependencies. The GW approximation is, in principle, a more improved method than the HF, since the HF corresponds to the ' $G^{\text{HF}}v$ ' approximation (the exchange term is given by the product of the Green function  $G^{\text{HF}}$  and the bare Coulomb interaction). Therefore, the GW approximation is free from the self-interaction correction.

For clusters, the quasiparticle energies for the lowest-unoccupied states are found to give reasonable electron affinities. It is often difficult to calculate the total energies

of the negatively charged systems. In finite systems, the highest occupied states of the negative systems are in general diffusive as in the case of  $\text{Na}_2$ ,  $\text{K}_2$ ,  $\text{Na}_3$  and  $\text{K}_3$ . This is a serious problem in the LDA. Therefore, it is more difficult to calculate the electron affinities than the ionization potentials. Thus, the GW quasiparticle approximation is a powerful tool for calculating the electron affinities and the excitation energies of an electron to the higher states.

In the present calculation, the quasiparticle energies are assumed to be real. It is, however, a very interesting problem to determine the lifetime of quasiparticles in alkali-metal clusters. Neither the density-functional theory nor quantum-chemical calculations, including the HF and the configuration interaction method, gives the lifetime of the quasiparticle. The calculation of the complex quasiparticle energies in the GW approximation (or beyond the GW) would reveal more of the validity and the limitations of the shell concept for alkali-metal clusters. Furthermore, unlike the SIC, the GW quasiparticle method is a well-founded approximation based on standard many-body theory. Therefore, further improvement is possible if necessary.

## 5. Summary and conclusion

In this work, we have calculated the quasiparticle energies of sodium and potassium clusters in the GW approximation for the self-energies of the valence electrons with the jellium-sphere-background model for ion cores. The occupied quasiparticle states obtained are considerably deeper than the LDA eigenstates, giving much better ionization potentials with the correct size dependence. The lowest-unoccupied quasiparticle states are, on the other hand, shallower than in the LDA and also give better electron affinities. Therefore, the GW approximation as implemented is found to describe quantitatively the one-particle properties in finite systems as well as in extended systems.

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## Appendix

In spherical systems, physical values can be expanded using Legendre functions  $P_l$ . We summarize here the equations for calculating the quasiparticle energies for spherical systems.

The LDA independent-particle density–density response function is given by

$$\begin{aligned} \chi_l^0(r_1, r_2; E) &= 2 \sum_{n, l'}^{\text{occ}} \frac{2l' + 1}{4\pi} R_{nl'}(r_1) R_{nl'}(r_2) \\ &\times \sum_{k=0}^{\min(l, l')} A_{ll'k} [G_{l+l'-2k}^R(r_1, r_2; E_{nl'} + E) \\ &+ G_{l+l'-2k}^{R*}(r_1, r_2; E_{nl'} - E)] \end{aligned} \quad (\text{A.1})$$

where [41, 42]

$$A_{ll'k} = \frac{a_{l'-k} a_k a_{l-k}}{a_{l+l'-k}} \frac{2l + 2l' - 4k + 1}{2l + 2l' - 2k + 1} \quad (\text{A.2})$$

$$a_n = \frac{(2n - 1)!!}{n!} \quad (\text{A.3})$$

and  $R_{nl}$  is the radial-part LDA wavefunction.  $G_l$  is the LDA Green function discussed in subsection 2.2. The TDLDA density–density response function satisfies

$$\begin{aligned} \chi_l^R(r_1, r_2; E) &= \chi_l^0(r_1, r_2; E) \\ &+ \int_0^\infty dr_3 \int_0^\infty dr_4 (r_3 r_4)^2 \chi_l^0(r_1, r_3; E) K_l(r_3, r_4) \chi_l^R(r_4, r_2; E). \end{aligned} \quad (\text{A.4})$$

By the square-matrix approximation (subsection 2.3),  $\chi_l^R(r, r'; iy_1)$  and  $\chi_l^R(r, r'; iy_2)$  give the excitation energies  $\omega_{nl}$  and

$$V_{nl}(r) = \int_0^\infty dr' (r')^2 v_l(r, r') N_{nl}(r'). \quad (\text{A.5})$$

Then, we can evaluate the screened Coulomb interaction as

$$W_l(r, r'; E) = v_l(r, r') + \sum_n V_{nl}(r) \left( \frac{1}{E - \omega_{nl} + i\eta} - \frac{1}{E + \omega_{nl} - i\eta} \right) V_{nl}(r'). \quad (\text{A.6})$$

The self-energy is given by

$$\begin{aligned} \Sigma_l(r, r'; E) &= - \sum_{n, l'}^{\text{occ}} \frac{2l' + 1}{4\pi} R_{nl'}(r) R_{nl'}(r') \sum_{k=0}^{\min(l, l')} A_{ll'k} W_{l+l'-2k}(r, r'; E - E_{nl'}) \\ &+ \sum_{n, l'}^{\text{occ}} \frac{2l' + 1}{4\pi} V_{nl'}(r) V_{nl'}(r') \sum_{k=0}^{\min(l, l')} A_{ll'k} G_{l+l'-2k}(r, r'; E - \omega_{nl'}). \end{aligned} \quad (\text{A.7})$$

Using the above self-energy operator, the quasiparticle energies are calculated self-consistently from

$$\begin{aligned} E_{nl} &= \epsilon_{nl} - \int_0^\infty dr r^2 R_{nl}(r) V_{xc} R_{nl}(r) \\ &+ \int_0^\infty dr \int_0^\infty dr' (rr')^2 R_{nl}(r) \Sigma_l(r, r'; E_{nl}) R_{nl}(r'). \end{aligned} \quad (\text{A.8})$$

In the actual calculation, all the functions of  $r$  (and  $r'$ ) are evaluated numerically on a discrete grid with uniform distance ( $\Delta r = 0.4$  au). The final grid point ( $r_{\max}$ ) in each case is determined from the condition  $V_{xc}(r_{\max}) < 10^{-3}$  (Ryd). The cut-off angular momentum,  $l_c$ , is also introduced for the sum over  $\omega_{nl}$  in (A.7). Results given in the present paper are converged with respect to  $\Delta r$ ,  $r_{\max}$  and  $l_c$  within 0.1 (eV).

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