

Ab initio GW quasiparticle calculation of small alkali-metal clusters

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***Ab initio* GW quasiparticle calculation of small alkali-metal clusters**Soh Ishii,¹ Kaoru Ohno,^{1,2,3} Yoshiyuki Kawazoe,¹ and Steven G. Louie²¹*Institute for Materials Research, Tohoku University, Katahira, Sendai 980-8577, Japan*²*Department of Physics, University of California, Berkeley, California 94720**and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*³*Department of Physics, Graduate School of Engineering, Yokohama National University, Tokiwadai, Yokohama 240-8501, Japan*

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Quasiparticle energies of small alkali-metal clusters (Li_n , Na_n , K_n ; $n=2,4,6,8$) are evaluated from first principles by means of the *GW* approximation with the generalized plasmon-pole model. An all-electron mixed-basis approach, in which wave function is represented as a linear combination of both plane waves and atomic orbitals, is adopted in the calculation. Obtained quasiparticle energies (ionization potential and electron affinity) are in good agreement with available experimental data.

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I. INTRODUCTION

Alkali-metal clusters have been widely studied since the 1980's both theoretically and experimentally.¹ Many *ab initio* theoretical studies have been performed on the basis of density functional theory² within the local density approximation (LDA)³ which has been recognized to be a very good approximation for ground state properties of materials. However, it has also been recognized that the energy gap between the LDA eigenvalues of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels is much smaller than the experimental energy gap. According to Koopmans theorem, the absolute value of the HOMO (LUMO) energy equals an ionization potential [an electron affinity (EA)], but the corresponding LDA eigenvalue of the HOMO level underestimates the experimental ionization potential and that of the LUMO level overestimates the experimental electron affinity. As a result, the energy gap estimated from the LDA eigenvalues becomes much smaller than that of the experimental value. This is because one cannot directly interpret LDA eigenvalues as one-particle quasiparticle energies (cf. Janak theorem).

It has been recognized that the effect of the self-energy corrections is important to reproduce the energy gap of molecules.⁴ This is also at the origin of bad descriptions of three electron-two center systems recently discussed by Chermette *et al.*⁵ It can be cured in a simple approximate way through the Slater's transition state approach, as shown recently by Liberman.⁶ In addition, there are two methods to evaluate the quasiparticle energies such as ionization potential (IP) (EA) correctly. One is to calculate the total energies of neutral and positively (negatively) charged system and to take the energy difference (for IP of lithium clusters, see Ref. 7). However, three times calculations of total energy are needed for the evaluation of both IP and EA and the results for IP are about 0.2 eV off from the experimental values. Another method is the Green's function approach, going beyond the ground state.

One such theory is the *GW* approximation (GWA)^{8,9} for the one-electron self-energy. Saito *et al.*¹⁰ performed *GW* calculations for sodium and potassium clusters by using a

jellium background model. The state-of-the art *GW* calculations for real inhomogeneous systems were first performed by Hybertsen and Louie⁹ and later by Godby *et al.*¹¹ for many typical semiconductors. Since then, many calculations have been successfully done for various crystalline semiconductors and insulators, and their surfaces.¹² In contrast to these studies on bulk systems, there has been published only a limited number of papers for isolated systems so far. By means of a pseudopotential plane wave approach, Shirley and Martin¹³ performed *GW* calculation for atoms, and Onida *et al.*¹⁴ calculated Na_4 . Rohlfing and Louie^{15,16} performed calculations on Si_nH_m clusters and conjugated polymers, and Grossman *et al.*¹⁷ performed calculations on SiH_4 and CH_4 with a pseudopotential LCAO approach (Ref. 17 reports results from quantum Monte Carlo simulations also). In these calculations, one usually employs the generalized plasmon-pole (GPP) model as first introduced by Hybertsen and Louie⁹ to approximate the frequency dependence of the dielectric function $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$. Recently we have performed *GW* calculations for small sodium clusters (Na_2 – Na_8) by using an all-electron mixed-basis approach and a full frequency integration.¹⁸

In the present paper, we perform similar *GW* calculation for the quasiparticle energies of small lithium and potassium clusters as well as sodium clusters by using the GPP model. Since we perform spin-independent calculations, we focus on the clusters with an even number of atoms. For lithium and sodium clusters, we compare the present result with the result obtained by the numerical integration. The rest of this paper is organized as follows: The computational method is briefly described in Sec. II. For further details of the methodology, one may refer to Ref. 18. In Sec. III, results and discussion for (A) lithium, (B) potassium, and (C) sodium clusters are presented separately. Section IV is devoted to some concluding remarks.

II. METHODOLOGY

We employ the all-electron mixed-basis approach,¹⁹ which is a natural extension of the pseudopotential mixed-basis approach.²⁰ In this approach, a wave function is expanded by both plane waves and atomic orbitals in order to

deal with the core electrons accurately. We use a Herman–Skillman²¹ code on a radial logarithmic mesh to generate atomic orbitals. This approach has been successfully applied to crystals, molecules, and clusters.^{22–26}

In the GWA, the one-electron self-energy $\Sigma(\omega)$ [defined apart from the Hartree potential $U = \int \rho(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')d\mathbf{r}'$ of the electron–electron Coulomb interaction v] is given by

$$\Sigma(\omega) = \frac{i}{2\pi} \int G(\omega + \omega')W(\omega')e^{i\eta\omega'}d\omega', \quad (1)$$

where G and W denote, respectively, the one-particle Green's function and the dynamically screened Coulomb interaction; and η is a positive infinitesimal number. [For simplicity, we have suppressed the $(\mathbf{r}, \mathbf{r}')$ dependence of all quantities.] One can divide the self-energy into two parts; one corresponds to the bare-exchange energy

$$\Sigma_x = \frac{i}{2\pi} v \int G(\omega)e^{i\eta\omega}d\omega, \quad (2)$$

which can be evaluated as Eq. (9) of Ref. 18. The remaining $\Sigma_c(\omega)$ is related to the correlation energy and represented by Eq. (11) of Ref. 18 [it is defined as the residue after Σ_x is subtracted from Eq. (1)]. Writing the dielectric function and polarizability, respectively, as ϵ and P , one can derive $W = \epsilon^{-1}v$ from $\epsilon = 1 - vP$. Usually, the polarizability P is evaluated under the random phase approximation.

In principle, the Dyson equation,

$$[T + V + U + \Sigma(E_n^{\text{GWA}})]|n\rangle = E_n^{\text{GWA}}|n\rangle, \quad (3)$$

could be solved self-consistently, where T and V denote the kinetic energy operator and the Coulomb potential caused by the positive point charges of the nuclei, respectively. However, it is a very difficult task to solve the Dyson equation self-consistently. In addition, the self-consistent GW calculation does not always give reliable quasiparticle energies because the f -sum rule is not always guaranteed.²⁷ If one wants to get reliable quasiparticle energies, vertex corrections are needed.²⁷ In the present study, we use the LDA wave functions and eigenvalues to evaluate G and W from the viewpoint of perturbation theory. In determining quasiparticle energy within the GWA, one then has⁹

$$E_n^{\text{GWA}} = E_n^{\text{LDA}} + \frac{1}{1 - (\partial\Sigma(\omega)/\partial\omega)_{E_n^{\text{LDA}}}} \langle n | \Sigma(E_n^{\text{LDA}}) - \mu_{xc}^{\text{LDA}} | n \rangle, \quad (4)$$

where E_n^{LDA} and μ_{xc}^{LDA} are the LDA eigenvalue and exchange–correlation potential, respectively. Equation (4) has been widely used in the literature and is known to give good quasiparticle energies for moderately correlated electron systems.¹²

The atomic configuration of the Li and Na clusters studied here is referred to in Refs. 28–30 [see Fig. 1(a) for Li clusters and Fig. 1 of Ref. 18 for Na clusters].

We also checked that those structures of lithium and sodium clusters are most stable by using an *ab initio* total

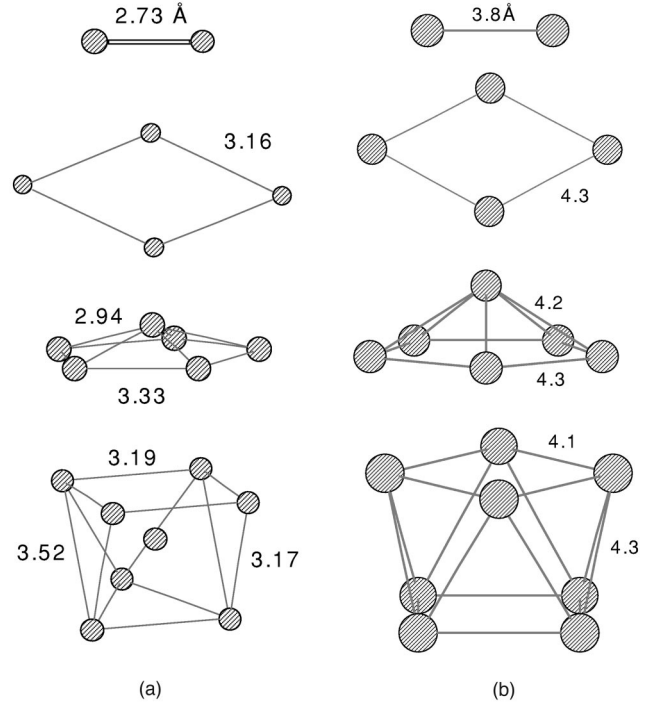


FIG. 1. The atomic configuration of (a) Li, which is referred to in Refs. 28 and 29, and that of (b) K clusters optimized in the present study.

energy method³¹ with ultrasoft pseudopotentials.³² Note that our optimized structures for Li_8 are different from that of Ref. 28, but the same as that of Ref. 29. For the potassium clusters, we obtained the optimized structure [Fig. 1(b)] by an *ab initio* total energy method³¹ with ultrasoft pseudopotentials³² within the LDA and a plane-wave basis. In the calculations, we employ a fcc supercell with a cubic edge of 50 and 70 a.u. for lithium and potassium clusters, respectively. In the calculation of $\Sigma_c(\omega)$, $1471\mathbf{G}(\mathbf{G}')$ for potassium or $645\mathbf{G}(\mathbf{G}')$ for lithium clusters (both roughly corresponding to 1-Ry cutoff energy) are required to achieve a good convergence of within 0.1 eV (note that the size of the supercell of potassium cluster is larger than that of lithium clusters). For the evaluation of Σ_x in Fourier space we need cutoff energy of 13–30 Ry to take into account the core contribution.

III. RESULTS AND DISCUSSION

In the present all-electron calculation, since μ_{xc} contains core contributions, the core contribution to the exchange part Σ_x of the self-energy cannot be ignored. In fact, for lithium dimer, the core contribution to the expectation value $\Sigma_{x,n} = \langle n | \Sigma_x | n \rangle$ for the HOMO state is about -0.7 eV, for example. On the other hand, the core contribution to the correlation part $\Sigma_c(\omega)$ can be ignored, because it is within the error bar (0.1 eV) of the present calculation.

A. Li clusters

Figure 2 shows the absolute value of the calculated LDA eigenvalue and GWA quasiparticle energies for the HOMO

TABLE I. Contributions to the quasiparticle energies (in eV) for the HOMO and LUMO levels of lithium clusters are shown in comparison with the experimental ionization potential and the electron affinity with negative signs (E_n^{exp})—Refs. 35 and 36. $\mu_{xc,n}^{\text{LDA}} = \langle n | \mu_{xc}^{\text{LDA}} | n \rangle$, $\Sigma_{x,n} = \langle n | \Sigma_x | n \rangle$, and $\Sigma_{c,n}(E_n^{\text{LDA}}) = \langle n | \Sigma_c(E_n^{\text{LDA}}) | n \rangle$ are the expectation values of, respectively, the LDA exchange–correlation potential, the exchange part [Eq. (2)], and the correlation part of the self-energy Σ . The final result E_n^{GWA} is evaluated through Eq. (4).

| | | E_n^{LDA} | $\mu_{xc,n}^{\text{LDA}}$ | $\Sigma_{x,n}$ | $\Sigma_{c,n}(E_n^{\text{LDA}})$ | E_n^{GWA} | E_n^{exp} |
|-----------------|------|--------------------|---------------------------|----------------|----------------------------------|--------------------|--------------------|
| Li ₂ | HOMO | −3.17 | −5.49 | −7.02 | −0.64 | −5.06 | −5.14 |
| | LUMO | −1.73 | −3.67 | −1.35 | −0.79 | −0.47 | −0.437±0.009 |
| Li ₄ | HOMO | −2.77 | −5.19 | −6.39 | −0.67 | −4.30 | −4.31±0.05 |
| | LUMO | −2.00 | −3.99 | −1.47 | −1.19 | −0.91 | |
| Li ₆ | HOMO | −3.03 | −5.44 | −6.54 | −0.44 | −4.25 | −4.20±0.05 |
| | LUMO | −1.81 | −4.03 | −1.39 | −1.53 | −0.94 | |
| Li ₈ | HOMO | −2.93 | −5.84 | −6.97 | −0.29 | −4.10 | −4.16±0.05 |
| | LUMO | −1.60 | −4.12 | −1.69 | −1.45 | −0.82 | |

(a) and LUMO (b) levels of lithium clusters [calculated with the GPP model and Eq. (4)], compared with the experimental ionization potential (IP)³³ and electron affinity (EA).³⁴ Although the LDA eigenvalue underestimates the IP by about 30%–50%, the *GW* quasiparticle energies are in excellent agreement with the experimental IP. Similarly, although the LDA eigenvalue overestimates the EA by about 300% for

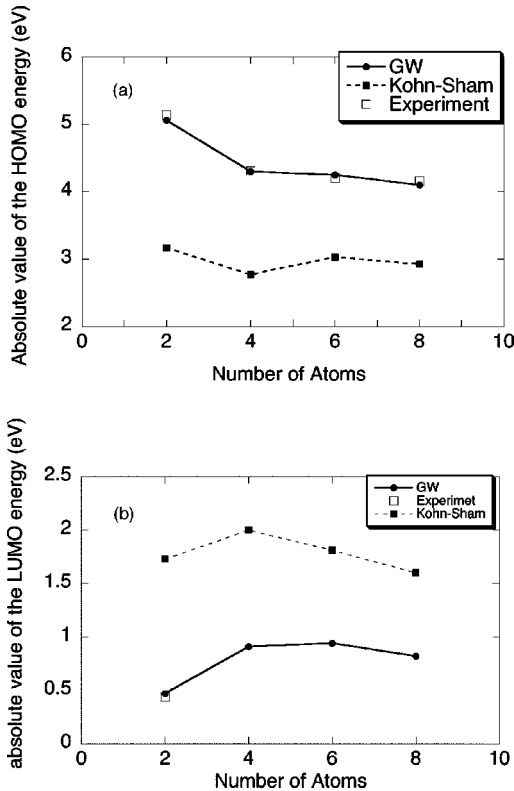


FIG. 2. Cluster size dependence of the absolute value of the quasiparticle energy E_n^{GWA} of lithium clusters evaluated by using the GPP model and Eq. (4). (a) The HOMO level corresponding to IP and (b) the LUMO level corresponding to EA. For comparison, experimental ionization potential (Ref. 33) and electron affinity (Ref. 34) are also shown, respectively, in (a) and (b).

lithium dimer, the *GW* quasiparticle energy reproduces experimental EA very well.

Table I lists the separate contributions to the *GW* quasiparticle energies for the HOMO and LUMO levels of lithium clusters, as well as the final result (E_n^{GWA}) calculated with Eq. (4). The listed contributions, E_n^{LDA} , $\mu_{xc,n}^{\text{LDA}}$, $\Sigma_{x,n}$, and $\Sigma_{c,n}(E_n^{\text{LDA}})$, represent the expectation values of, respectively, the LDA Hamiltonian ($H^{\text{LDA}} = T + V + U + \mu_{xc}^{\text{LDA}}$), the LDA exchange–correlation potential (μ_{xc}^{LDA}), and the exchange and correlation parts of the self-energy [Σ_x and $\Sigma_c(E_n^{\text{LDA}})$ evaluated with the GPP model]. The absolute values ($|E_n^{\text{GWA}}|$) of the HOMO and LUMO quasiparticle energies correspond to the IP and EA, respectively. For comparison, experimentally reported IP and EA (for adiabatic and vertical transitions)^{33,34} with negative signs, corresponding to E_n^{exp} , are also listed in Table I.

For comparison to the GPP model, we also performed the full numerical ω' integration of the self-energy in Eq. (1) for Li_{*n*} ($n = 2, 4, 6, 8$). The technical details of this calculation are the same as those explained in Ref. 18. The expectation value $\Sigma_{c,n}(E_n^{\text{LDA}})$ of the correlation part of the self-energy is evaluated with numerical integration and compared with the value evaluated with the GPP model in Table II. From Table

TABLE II. Cluster size dependence of the correlation term of the self-energy [$\Sigma_{c,n} = \langle n | \Sigma_c(E_n^{\text{LDA}}) | n \rangle$, in units of eV] for lithium clusters calculated by employing either the GPP model or the numerical integration.

| | | GPP model | Numerical integration |
|-----------------|------|-----------|-----------------------|
| Li ₂ | HOMO | −0.64 | −0.66 |
| | LUMO | −0.79 | −0.81 |
| Li ₄ | HOMO | −0.67 | −0.68 |
| | LUMO | −1.19 | −1.20 |
| Li ₆ | HOMO | −0.44 | −0.46 |
| | LUMO | −1.53 | −1.42 |
| Li ₈ | HOMO | −0.29 | −0.37 |
| | LUMO | −1.45 | −1.46 |

TABLE III. Contributions to the quasiparticle energies (in eV) for the HOMO and LUMO levels of potassium clusters are shown as well as the final result and the experimental IP and EA with negative signs—Refs. 35 and 36 (for the E_n^{exp} of the LUMO level corresponding to EA, symbols (v) and (a) indicate, respectively, the vertical and adiabatic transitions—Ref. 36).

| | | E_n^{LDA} | $\mu_{xc,n}^{\text{LDA}}$ | $\Sigma_{x,n}$ | $\Sigma_{c,n}(E_n^{\text{LDA}})$ | E_n^{GWA} | E_n^{exp} |
|----------------|------|--------------------|---------------------------|----------------|----------------------------------|--------------------|--------------------------------------|
| K ₂ | HOMO | -2.55 | -4.90 | -5.67 | -0.74 | -3.84 | -4.05±0.05 |
| | LUMO | -1.64 | -3.83 | -1.90 | -0.70 | -0.72 | -0.550±0.010 (v) -0.493±0.012 (a) |
| K ₄ | HOMO | -2.29 | -4.94 | -5.44 | -0.78 | -3.29 | -3.6±0.1 |
| | LUMO | -1.97 | -4.23 | -1.96 | -0.89 | -0.88 | -1.048±0.025 (v) -0.83±0.12 (a) |
| K ₆ | HOMO | -2.51 | -5.21 | -5.62 | -0.62 | -3.30 | -3.35±0.03 |
| | LUMO | -1.81 | -4.30 | -1.99 | -1.01 | -0.81 | -1.091±0.020 (v) -0.95±0.10 (a) |
| K ₈ | HOMO | -2.46 | -5.22 | -5.52 | -0.66 | -3.21 | -3.4±0.1 |
| | LUMO | -1.59 | -4.57 | -2.39 | -0.94 | -0.68 | ~ -0.85 |

II, we observe that as in previous studies for bulk systems the GPP model is a very good approximation to reproduce the electron self-energy.

In Table I, we note that $\Sigma_{x,n}$ of the HOMO level of lithium clusters is larger than that of potassium and sodium clusters (see Secs. III B and III C and Tables III and IV). This is because both the bond length and the core radius of Li clusters are smaller than those of K and Na clusters, leading to stronger overlap between the more localized wave functions.

One would expect that, as the cluster size is increased, the absolute value of $\Sigma_{x,n}$ of the HOMO level becomes smaller because the wave functions of the occupied levels become more delocalized, and that of the LUMO level becomes larger because overlap between wave functions of the HOMO and LUMO levels increases. This statement is approximately correct for Li_n, Na_n, and K_n except for the case of $n=4$ where the structure is a spatially spread rhombohedron. Another exception is Li₈, whose $\Sigma_{x,n}$ of the HOMO level is deeper than that of Li₄ and Li₆ and is comparable to that of Li₂.

This irregular behavior of Li₈ may be attributed to its structure, the centered trigonal prism,²⁹ which is quite different from that of potassium and sodium clusters. Lithium atom has no p orbitals in occupied levels. This makes the energy of $2p$ orbitals deeper than that of sodium and potassium. Therefore, sp hybridization may take place more easily than the case of sodium and potassium. In the structure of Li₈, the central atom's p orbitals are partially occupied and it is negatively charged with the charge of nearly $-e$. The surface atoms are positively charged. Hence, the wave function of the HOMO level is localized at the central atom, and makes $\Sigma_{x,n}$ of the HOMO level of Li₈ relatively larger compared to those of the other clusters.

Concerning the correlation part of the self-energy, one should note that the absolute value of $\Sigma_{c,n}(E_n^{\text{LDA}})$ of the HOMO level is relatively small for Li₆ and Li₈. This can be attributed again to the localized character of the HOMO

wave function, because screening becomes ineffective for short distances in the region where the wave function is localized.

To see the sensitivity of the quasiparticle energies to the structural geometry, we performed also the GW calculation for Li₈ with T_d symmetry, which is referred to in Ref. 29. Obtained IP for this cluster is about 4.5 eV and less agreement with experiment as in the result given in Ref. 7. This structure is not stable energetically.²⁹

B. K clusters

Table III lists each contribution to the GW quasiparticle energy in the case of potassium clusters, as is the same way in Table I. For comparison, the experimental IP and EA (Refs. 35 and 36) with minus signs are also shown in Table I. Again, the absolute value of the HOMO (LUMO) level energy corresponds to the IP (EA). Similar to lithium clusters, LDA eigenvalues underestimate the IP by about 30%–50% and overestimate the EA by about 200%–300%. The agreement between the present GW result and experimental data is much better (although not as good as the result for lithium clusters presented in Sec. III A).

From Table III, it is seen that absolute value of $\Sigma_{x,n}$ of the HOMO level becomes smaller with increasing cluster size (except for K₄ with a rhombohedron structure), while that of the LUMO level remains almost the same except for K₈. The same tendency is also seen in sodium clusters¹⁸ and the reason for this trend was already explained in Sec. III A. The reason why $\Sigma_{x,n}$ of the LUMO level is deeper in K₈ may be explained as follows (see also Ref. 18): The geometry of K₈ is D_{4d} , which is the same as that of Na₈ in Ref. 18. The representation of the LUMO level is given by $1E_3$ and is similar to that of the HOMO and HOMO-1 levels whose representations are given by $1B_2$ and $1E_1$, respectively. Because of this fact, overlap of these three states is large, and, therefore, $\Sigma_{x,n}$ of K₈ of the LUMO level is deeper than that of the other potassium clusters studied here.

TABLE IV. The correlation part [$\Sigma_{c,n}(E_n^{\text{LDA}})$] of the self-energy for sodium clusters calculated by employing either the GPP model (present result) or the numerical integration (in parentheses)—Ref. 18. All other contributions to the quasiparticle energies are the same as those listed in Table II of Ref. 18. The final result (E_n^{GWA}) is compared to the experimental IP and EA with negative signs (E_n^{exp})—Refs. 35–37. For the E_n^{exp} for the LUMO level corresponding to EA, symbols (v) and (a) indicate, respectively, the vertical and adiabatic transitions (Ref. 36). The values without and with parentheses are results from using the GPP model and full frequency numerical integration, respectively. All numbers are given in units of eV.

| | | $\Sigma_{c,n}(E_n^{\text{LDA}})$ | E_n^{GWA} | E_n^{exp} |
|-----------------|------|----------------------------------|--------------------|--------------------------------------|
| Na ₂ | HOMO | -0.71(-0.73) | -4.88(-4.90) | -4.9328±0.001 |
| | LUMO | -0.66(-0.66) | -0.63(-0.63) | -0.543±0.010 (v) -0.430±0.015 (a) |
| Na ₄ | HOMO | -0.90(-1.01) | -3.85(-3.96) | -4.268±0.054 |
| | LUMO | -1.23(-1.35) | -1.00(-1.12) | -1.145±0.030 (v) -0.91±0.15 (a) |
| Na ₆ | HOMO | -0.69(-0.86) | -3.78(-3.95) | -4.118±0.054 |
| | LUMO | -1.49(-1.53) | -1.21(-1.25) | |
| Na ₈ | HOMO | -0.70(-0.85) | -3.80(-3.95) | -4.05±0.054 |
| | LUMO | -1.25(-1.40) | -0.83(-0.98) | |

C. Na clusters

Since we presented explicit values of each contribution to the GW quasiparticle energy of sodium clusters already in Table II of our previous paper,¹⁸ we do not present them here again. All the contributions are the same in the present study except for $\Sigma_{c,n}(E_n^{\text{GWA}})$, which was evaluated with the full numerical integration in Ref. 18 and now is evaluated with the GPP model.

In first column of Table IV, $\Sigma_{c,n}$ calculated with the GPP model is compared with corresponding value calculated with the full frequency numerical integration (inside the parentheses). From this, we see that the difference between the GPP model and the numerical integration is at most 0.15 eV.

The final quasiparticle energies (E_n^{GWA}) are shown in the next column in Table IV. Here, the values in parentheses are

results from numerical integration. The experimental IP and EA with negative signs (E_n^{exp})^{35–37} are also shown for comparison.

IV. CONCLUDING REMARKS

We have carried out GW calculations for small lithium, sodium, and potassium clusters by using the GPP model to evaluate the self-energy. Using the all-electron mixed-basis approach, we found that in an all-electron calculation the core contribution is essential in the evaluation of the exchange part Σ_x of the self-energy, although it can be ignored in the evaluation of the correlation part Σ_c . The GPP model turns out to be a fairly good approximation. It reproduces the value of the numerical integration (1) with an error of 0.15 eV at most. Although the LDA eigenvalue underestimates the experimental ionization potential and overestimates the electron affinity, the GW quasiparticle energy obtained in the present study is in good agreement with available experimental data for all clusters. The overall cluster-size dependence of the IP and EA is similar between potassium and lithium clusters, but the exchange and correlation contributions to the self-energy [i.e., $\Sigma_{x,n}$ and $\Sigma_{c,n}(E_n^{\text{LDA}})$] are different between the two species. As discussed in Sec. III, the behavior of each contribution is well understood in relation to the cluster size and structure.

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