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A state-of-the-art GW calculation is carried out for small sodium clusters, Na_2, Na_4, Na_6, and Na_8. The quasiparticle energies are evaluated by employing an *ab initio GW* code based on an all-electron mixed-basis approach, which uses both plane waves and atomic orbitals as basis functions. The calculated ionization potential and the electron affinity are in excellent agreement with available experimental data. The exchange and correlation parts to the electron self-energy within the GW approximation are presented from the viewpoint of their size dependence. In addition, the effect of the off-diagonal elements of the self-energy corrections to the local-density-approximation exchange-correlation potential is discussed. Na_2 and Na_8 have a larger energy gap than Na_4 and Na_6, consistent with the fact that they are magic number clusters.

I. INTRODUCTION

Alkali-metal clusters have been studied widely since the 1980's.[1] Earlier theoretical studies were based on the Hückel model, shell model, and *ab initio* pseudopotential approaches.[2] The stability of simple metal clusters has been investigated by several approaches.[1] Röthlisberger and Andreoni[3] investigated the stability of Na_n ($n=2–20$) for many structures within the local density approximation (LDA). Saito *et al.*[5,6] determined the quasiparticle energies of Na_n and K_n ($n=2, 8, 18, 20,$ and 40) within the GW approximation[4] (GWA) based on a simplified jellium-background model. Onida *et al.*[7] calculated the absorption spectrum of Na_4 starting from the *ab initio* GWA. Vasiliev *et al.*[8] evaluated the absorption spectrum of small sodium clusters using the time-dependent local density approximation.

The local density approximation based on density functional theory[9,10] is a very good approximation for describing the electronic ground state of materials. However, excitation energies obtained within the LDA via the Koopmans theorem do not agree with experiments. For example, the LDA significantly underestimates the band gap of semiconductors and the ionization potential of alkali-metal clusters. One of the methods for evaluating the quasiparticle excitation energies correctly is the GWA, introduced by Hedin[4] from the viewpoint of many-body quantum field theory. Calculations for real materials based on the *ab initio* GWA were carried out by Hybertsen and Louie.[11,12] Similar calculations have subsequently been performed for many systems, employing various methods including linear combination of atomic orbitals,[13] linear muffin-tin orbitals,[14] and plane wave expansion.[11,12,15,16] Large calculations of this type were done, for example, for C_{60} by Shirley and Louie[17] and by Gunnarsson.[18] Recently, total energy calculations within the GWA have been performed by Holm[19] and by Holm and Aryasetiawan.[20]

However, most of these calculations are based on certain approximations such as pseudopotentials for the electron-core interaction, a generalized plasmon-pole model,[12] or a model using empirical parameters[18] to evaluate the dielectric function. The ω dependence of the linear-response function, for example, was calculated by Miyake and Aryasetiawan.[21] The aim of the present paper is to evaluate *the quasiparticle energies within the GWA using an all-electron method and a full ω-dependent* random-phase-approximation (RPA) *dielectric function*. In particular, we study the ionization potential (IP) and electron affinity (EA) of Na_n ($n=2,4,6,8$) clusters. For this purpose, we use a code based on the all-electron mixed-basis approach.[22,23] The all-electron approach was adopted for evaluating the plasmon lifetime in potassium by Ku and Eguiluz.[24]

The mixed-basis approach was successfully used by Louie, Ho, and Cohen[25] in order to treat localized d orbitals within the pseudopotential method. The present all-electron mixed-basis approach is a natural extension of the pseudopotential method to take the core electrons fully into account. The crystal wave functions are expanded using the atomic core orbitals and plane waves. The core wave functions are primarily expressed by the atomic core orbitals of isolated atoms. The atomic wave functions are evaluated using the Herman-Skillman code[26] on a radial logarithmic mesh, which allows an accurate description in the vicinity of nuclei. We replace the potential experienced by the core atomic orbitals with its spherically averaged value, since the core region is usually very small and the potential is mostly spherically symmetric around nuclei. Then all matrix elements are accurately evaluated by using fast Fourier transformation and a one-dimensional integral along the radial (logarithmic) mesh. The present all-electron mixed-basis approach has already been successfully applied to *ab initio* calculations of the magnetic susceptibility,[27] dielectric function,[28] and also to *ab initio* molecular dynamics.[29–31]

II. *GW* APPROXIMATION

The GWA has been explained in Refs. 4 and 12 in detail. For the general case of an inhomogeneous system, the quasiparticle energies $E_{n,\mathbf{k}}$ and wave functions $\psi_{n,\mathbf{k}}(\mathbf{r})$ are obtained by solving the equation

$$(T+V_{ext}+V_H)\psi_{n,\mathbf{k}}(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_{n,\mathbf{k}})\psi_{n,\mathbf{k}}(\mathbf{r}')$$

$$=E_{n,\mathbf{k}}\psi_{n,\mathbf{k}}(\mathbf{r}), \tag{1}$$

where T, V_{ext}, V_H, and Σ are the kinetic energy operator, external potential, Hartree potential, and the electron self-energy operator containing the effect of exchange and correlation between electrons, respectively. In the *GW* approximation, Σ is taken to be the first term in an expansion in the screened Coulomb interaction W:

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

The one-particle Green's function G is given by

$$G(\mathbf{r},\mathbf{r}',\omega)=\sum_{n'}\frac{\psi_{n'}(\mathbf{r})\psi_{n'}^*(\mathbf{r}')}{\omega-E_{n'}\pm i\delta}, \tag{3}$$

where to a good approximation $\psi_n(\mathbf{r})$ and E_n may be taken as the LDA wave functions and the LDA energy eigenvalues, respectively, and δ is a positive infinitesimal number. The sign in front of δ is negative when the level n' is occupied, and positive when n' is empty. One could also use self-consistently the resulting quasiparticle energies for E_n, although the results usually do not change significantly. The dynamically screened Coulomb interaction W is given in Fourier space by

$$W_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)=[\epsilon^{-1}]_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)v(\mathbf{q}+\mathbf{G}'), \tag{4}$$

where $v(\mathbf{q}+\mathbf{G})=4\pi/|\mathbf{q}+\mathbf{G}|^2$ is the Coulomb potential in Fourier space and $\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ is the dielectric matrix defined by

$$\epsilon_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)=\delta_{\mathbf{G},\mathbf{G}'}-v(\mathbf{q}+\mathbf{G})P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) \tag{5}$$

with the polarizability function (in the RPA)

$$P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)=\sum_{\mathbf{k}}\left[\sum_{n}^{occ}\sum_{n'}^{emp}\frac{\langle n,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},n'\rangle\langle n',\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|\mathbf{k},n\rangle}{E_{n,\mathbf{k}}-E_{n',\mathbf{k}+\mathbf{q}}-\omega+i\delta}\right.$$

$$\left.-\sum_{n}^{emp}\sum_{n'}^{occ}\frac{\langle n,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\mathbf{k}+\mathbf{q},n'\rangle\langle n',\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|\mathbf{k},n\rangle}{E_{n,\mathbf{k}}-E_{n',\mathbf{k}+\mathbf{q}}-\omega-i\delta}\right]. \tag{6}$$

Here $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors, δ is positive infinitesimal, and *occ* (*emp*) means that the summations run over all occupied (empty) levels. $P_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ is an even function of ω. Some models, such as the generalized plasmon-pole model[12] or those using experimental parameters,[16] could be used to bypass the calculation of the ω dependence of the dielectric matrices in order to reduce the time of computation. Here, we calculate the ω dependence of the dielectric matrices explicitly. The Fourier transform of Eq. (4) to real space is then

$$W(\mathbf{r},\mathbf{r}';\omega)=\sum_{\mathbf{q}}\sum_{\mathbf{G},\mathbf{G}'}e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}W_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}. \tag{7}$$

The screened Coulomb interaction W may be divided into two parts, $W=W_c+v$, where the second term v denotes the bare Coulomb interaction. Hence, the self-energy operator Σ may also be divided into two terms. One is the Fock exchange term

$$\Sigma_x(\mathbf{r},\mathbf{r}')=\frac{i}{2\pi}v(\mathbf{r}-\mathbf{r}')\int e^{i\omega'\eta}G(\mathbf{r},\mathbf{r}';\omega')d\omega'. \tag{8}$$

The diagonal part of Σ_x in the LDA orbital basis can be rewritten as

$$\Sigma_{x,n}=\langle\psi_n(\mathbf{r})|\Sigma_x(\mathbf{r},\mathbf{r}')|\psi_n(\mathbf{r}')\rangle$$

$$=-\int d\mathbf{r}\int d\mathbf{r}'\sum_{m}\frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{9}$$

The other term represents a correlation term, which is given by

$$\Sigma_c(\mathbf{r},\mathbf{r}';\omega)=\frac{i}{2\pi}\int d\omega' e^{i\omega'\eta}G(\mathbf{r},\mathbf{r}';\omega+\omega')$$

$$\times[W(\mathbf{r},\mathbf{r}';\omega')-v(\mathbf{r}-\mathbf{r}')], \tag{10}$$

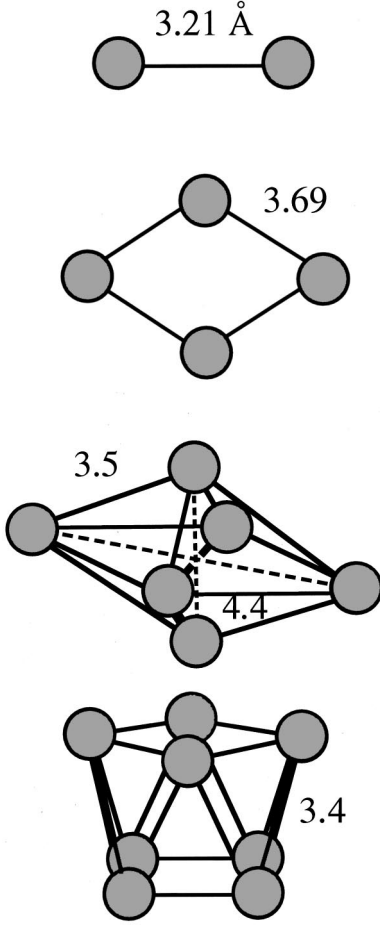and its diagonal matrix element becomes

FIG. 1. Structures of sodium clusters used in this work. These are referred to in Refs. 3 and 35. The numbers indicate the bond lengths in units of Å.

$$\Sigma_{c,n} = \langle n,\mathbf{k}|\Sigma_c(\mathbf{r},\mathbf{r}';\omega)|n,\mathbf{k}\rangle$$

$$= \sum_{n'} \sum_{\mathbf{q}} \sum_{\mathbf{G},\mathbf{G}'} \langle n,\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|n',\mathbf{k}-\mathbf{q}\rangle$$

$$\times \langle n',\mathbf{k}-\mathbf{q}|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|n,\mathbf{k}\rangle i \int_0^\infty \frac{d\omega'}{2\pi} \{W_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega')$$

$$-\delta_{\mathbf{G},\mathbf{G}'} v(\mathbf{q}+\mathbf{G})\} \left\{ \frac{1}{\omega+\omega'-E_{\mathbf{k}-\mathbf{q},n'}-i\delta_{\mathbf{k}-\mathbf{q},n'}} \right.$$

$$\left. + \frac{1}{\omega-\omega'-E_{\mathbf{k}-\mathbf{q},n'}-i\delta_{\mathbf{k}-\mathbf{q},n'}} \right\} \qquad (11)$$

with the help of $W(\omega)=W(-\omega)$. This term represents the contribution related to the electron correlation. The quasiparticle energies may then be obtained in first-order perturbation as

$$E_n^{\mathrm{GWA}} \approx E_n + \int d\mathbf{r} \int d\mathbf{r}' \psi_n^*(\mathbf{r})$$

$$\times [\Sigma(\mathbf{r},\mathbf{r}',E_n) - \mu_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')]\psi_n(\mathbf{r}'). \qquad (12)$$
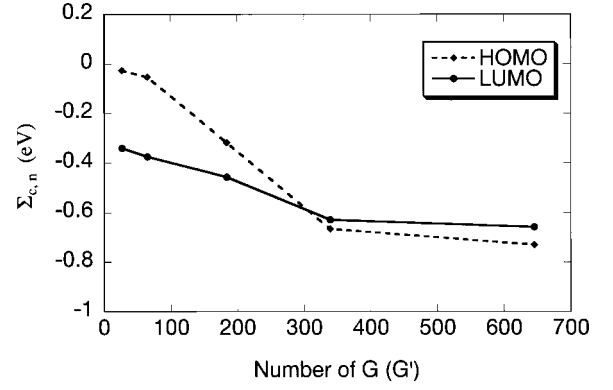

FIG. 2. The matrix-size dependence of the correlation part of the self-energy ($\Sigma_{c,n}$) of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) states of Na_2 in units of eV. The horizontal axis represents the size of the dielectric matrix, i.e., the number of the reciprocal lattice vector $\mathbf{G}$ or $\mathbf{G}'$ in Eq. (11).

Here $\mu_{\mathrm{xc}}^{\mathrm{LDA}}$ is the exchange-correlation potential in the LDA. In this study, we employ the Ceperley-Alder exchange-correlation potential.[32] It was recently claimed that using a fully self-consistent calculation instead of Eq. (3) leads to worse quasiparticle energies.[33] However, in such a calculation, the *f*-sum rule is not always guaranteed and vertex correction is needed.[34] Hereafter we will use Eq. (3), i.e., a quasiparticle approximation for **G**.

III. RESULTS AND DISCUSSION

The structures of clusters used in the present study are shown in Fig. 1 and given in Refs. 3 and 35. In the calculations, we employ a fcc supercell with a cubic edge of 50 a.u., which is chosen carefully to obtain convergence of absolute LDA energy levels. We also introduce a spherically truncated Coulomb potential, which is explained in Ref. 7, to avoid interaction between the cells. All calculations are performed for only the Γ point, corresponding to $\mathbf{q}=\mathbf{0}$. This is sufficient when the supercell is chosen sufficiently large. In our calculation, we confirmed that our result does not change even if we introduce **q**-point sampling. The size of the dielectric matrix given by Eq. (4) is chosen to be 645×645, which we found necessary and sufficient for all cases. Local-field corrections play a significant role in the evaluation of the correlation part of the self-energy, $\Sigma_{c,n}$. In fact, for the case of Na_2, for example, when the size of this matrix is chosen to be 65×65, $\Sigma_{c,n}$ of the highest occupied (lowest unoccupied) molecular orbital [HOMO (LUMO)] level is -0.05 eV $(-0.37$ eV), while the correct value is -0.73 eV $(-0.66$ eV). Figure 2 shows the matrix-size dependence of $\Sigma_{c,n}$ for the HOMO and LUMO levels of Na_2. The number of empty states required for the summation in Eq. (11) is 600 to achieve a good convergence. The contour of the ω' integral in Eq. (11) is chosen on the positive real axis ($0\leq\omega'\leq14$ eV) with the help of $W(\omega)=W(-\omega)$. We have carefully confirmed that this region of integration and the frequency interval of 0.25 eV are sufficient with the condition $\delta=0.01$ a.u. The core contribution to Σ_c is negligible, while the core contribution to Σ_x is important. In the com-

TABLE I. The contributions to the quasiparticle energies (in eV) for the HOMO and LUMO are shown compared with the experimental ionization potential and the negative of the electron affinity ($-E^{\text{exp}}$) (Refs. 36 and 37). $\mu_{\text{xc},n}^{\text{LDA}}=\langle \mathbf{k},n|\mu_{\text{xc}}^{\text{LDA}}|\mathbf{k},n\rangle$, $\Sigma_{\text{x},n}$ [Eq. (9)], and $\Sigma_{\text{c},n}$ [Eq. (11)] are the Kohn-Sham exchange correlation energy of the LDA and the exchange part and the correlation part of the self-energy Σ, respectively.

		E_n^{LDA}	$\mu_{\text{xc},n}^{\text{LDA}}$	$\Sigma_{\text{x},n}$	$\Sigma_{\text{c},n}$	E^{GWA}		E^{exp}
Na_2	HOMO	-3.14	-5.45	-6.66	-0.73	-5.08		-4.9328 ± 0.001
	LUMO	-1.89	-4.23	-2.02	-0.66	-0.33	$(-0.43)^{\text{a}}$	-0.430 ± 0.015
Na_4	HOMO	-2.62	-5.30	-5.92	-1.01	-4.25		-4.268 ± 0.054
	LUMO	-2.10	-4.48	-2.01	-1.35	-0.98		-0.91 ± 0.15
Na_6	HOMO	-2.71	-5.65	-6.24	-0.86	-4.16		-4.118 ± 0.054
	LUMO	-2.19	-4.81	-2.12	-1.53	-1.03		
Na_8	HOMO	-2.83	-5.74	-6.21	-0.85	-4.15		-4.05 ± 0.054
	LUMO	-1.58	-4.93	-2.73	-1.40	-0.78		

[a] $E^{\text{GWA}}=-0.33$ eV for the LUMO level of Na_2 becomes deeper by -0.1 eV and the agreement with $E^{\text{exp}}=-0.43\pm0.015$ becomes better if we rediagonalize the left-hand side of Eq. (1) by taking into account the off-diagonal elements of $\langle \mathbf{k},n|\Sigma-\mu_{\text{xc}}^{\text{LDA}}|\mathbf{k},n'\rangle$.

putation of $\Sigma_{\text{x},n}$, two-center integrals associated with only atomic orbitals on the same site (and not with plane waves) are evaluated in real space along the radial coordinate. All the rest of the contributions are evaluated in Fourier space with a cutoff energy of 30 Ry. As a test, we have calculated $\Sigma_{\text{x},n}$ of an isolated sodium atom using the supercell approach. The value obtained for the HOMO level is -6.99 eV, which is in good agreement with the value of -7.01 eV evaluated by the Herman-Skillman atomic code.[26] The core contribution to this value is -0.81 eV, which cannot be ignored.

The absolute value of the quasiparticle energy at the HOMO level is the IP. Similarly, the absolute value of the LUMO quasiparticle energy is the EA. Table I shows the HOMO and LUMO quasiparticle energies of sodium clusters obtained in the present study. For comparison, the LDA energy eigenvalues (E_n^{LDA}) and experimentally reported IP and EA values[36,37] with negative sign (E^{exp}) are listed in the same table. The separate contributions to the GW quasiparticle energies from the exchange and correlation parts of the self-energy are also shown.

First, it is found that, although the LDA Kohn-Sham HOMO eigenvalue underestimates the IP by about 30–50%, the GWA reproduces the experimental IP well. The absolute value of $\Sigma_{\text{x},n}$ of the HOMO level is about five times larger than that of $\Sigma_{\text{c},n}$. It tends to decrease when the size of the cluster increases, because the wave functions of valence electrons become delocalized. On the other hand, there is no major cluster-size dependence in $\Sigma_{\text{c},n}$ of the HOMO level.

Second, although the LDA Kohn-Sham eigenvalue overestimates the EA by about 200–500%, the absolute value of the GW LUMO energy is also in good agreement with available experimental data for the EA. Since Na_2 and Na_8 have a closed-shell structure, which makes the HOMO-LUMO gap larger, the EA of these clusters is smaller than that of the other clusters studied (for example, in the case of the potassium clusters the experimental EA of K_2 and K_8 is smaller than that of other clusters[37]). Concerning the cluster-size dependence of $\Sigma_{\text{x},n}$ of the LUMO level, it is almost constant

except for Na_8. The symmetry of Na_8 clusters studied is D_{4d}. The representation of the point group of the HOMO, the HOMO-1 state, and the LUMO state is $1B_2$, $1E_1$, and $1E_3$, respectively. $\Sigma_{\text{x},n}$ becomes large with increasing overlap between wave functions. In this case the character of the wave function of the LUMO state is similar to that of the HOMO-1 state because of its peculiar structure. $\Sigma_{\text{x},n}$ of the LUMO state of Na_8 is, therefore, larger than others studied by about 0.6 eV. On the other hand, the absolute value of $\Sigma_{\text{c},n}$ for the LUMO level tends to increase with increasing cluster size. This behavior stands in contrast to that of $\Sigma_{\text{c},n}$ for the HOMO level.

The resulting EA of Na_2 as calculated by first-order perturbation [Eq. (12)] is a little smaller than the experimental value. This is due to the fact that, if self-energy effects shift the quasiparticle energy closer to the vacuum level ($E=0$), above which the continuum spectrum of unbounded free-electron states exists, the quasiparticle wave functions may be considerably different from the Kohn-Sham orbitals. In such a case, one must calculate also off-diagonal elements of $\Sigma-\mu_{\text{xc}}^{\text{LDA}}$ (corresponding to calculating all the matrix elements of $\langle n|\Sigma-\mu_{\text{xc}}^{\text{LDA}}|m\rangle$) and solve the full Dyson's equation (corresponding to diagonalizing that matrix) to obtain more reliable quasiparticle energies and wave functions. This is because the quasiparticle wave functions become more extended than the LDA wave functions, due to the mixing with higher resonant LDA states through the interaction. We performed such a calculation for the dimer and found that this effect makes the LUMO quasiparticle energy deeper by about 0.1 eV while the HOMO quasiparticle energy remains unchanged. That is we find better agreement for the EA of Na_2 after inclusion of the effect of off-diagonal elements of $\Sigma-\mu_{\text{xc}}^{\text{LDA}}$. Such an effect is negligible, however, for clusters larger than Na_4, because the LUMO quasiparticle energy for these clusters is deeper.

The cluster-size dependence of the HOMO-LUMO gap energy is shown in Fig. 3. Onida *et al.* have reported that the HOMO-LUMO gap of Na_4 is 3.0 eV.[7] In contrast, our result is 3.3 eV. Na_2 and Na_8 have a larger HOMO-LUMO gap than other clusters, indicating that they are relatively stable.
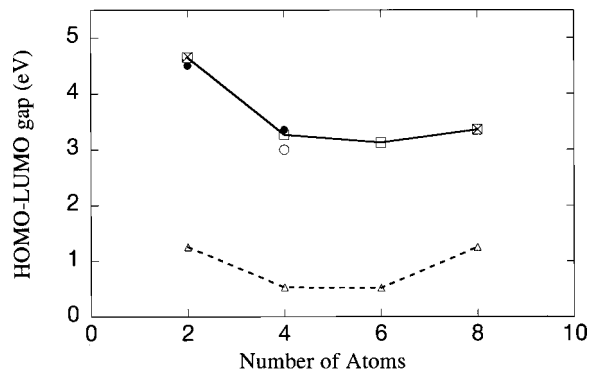
FIG. 3. The cluster-size dependence of the HOMO-LUMO gap (E_g in eV) obtained by the present *GW* calculations ($\square$), compared with the LDA Kohn-Sham eigenvalues ($\triangle$). Previous *GW* calculations based on a jellium-background model (Ref. 6) ($\times$) and an *ab initio* pseudopotential calculationn (Ref. 7) ($\bigcirc$) are also shown. In addition, the experimental HOMO-LUMO gaps calculated from the relation $E_g = \mathrm{IP} - \mathrm{EA}$ are shown ($\bullet$). The magic number clusters (Na_2 and Na_8) have a relatively larger gap.

$\Sigma_{x,n}$ plays a predominant role in enlarging the LDA gap. On the contrary, $\Sigma_{c,n}$ reduces it except for the case of the dimer (see Table I).

IV. CONCLUSION

We have successfully obtained the *ab initio GW* quasiparticle energies of Na_2, Na_4, Na_6, and Na_8 clusters by using an all-electron mixed-basis formulation and computer code. It is found that the present approach is particularly useful in determining the absolute values of quasiparticle energies of clusters, when a sufficiently large supercell is used. The frequency dependence of the dielectric response function within the RPA is calculated directly using the LDA results without relying on the generalized plasmon-pole model. The quasiparticle energies obtained by the GWA are in good agreement with available experimental data. In particular, local-field corrections are very important in improving quasiparticle energies. $\Sigma_{x,n}$ plays a major role in enlarging the HOMO-LUMO gap and making the HOMO energy deeper. The core contribution to $\Sigma_{x,n}$ is not negligible. Both $\Sigma_{x,n}$ and $\Sigma_{c,n}$ play important roles in reproducing the size dependence of the quasiparticle energies. If the self-energy corrections to the LDA LUMO make the quasiparticle energy approach the vacuum level from below, the corresponding LDA wave function will not be a good approximation to the quasiparticle wave function. We found that it requires calculation of the off-diagonal elements of $\Sigma - \mu_{xc}^{LDA}$ similar to what was found in Ref. 38. This is the case for the LUMO level (the EA) of Na_2.

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