Density Functional Theory with Optimized Effective Potential: An Application to Hollow Atoms in the Bulk of Metallic Materials

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The local spin-density functional theory with an optimized effective potential and self-interaction correction is used to study the energy structure of hollow atoms or ions in the bulk of metallic materials. The energy structure of conduction electrons in the bulk of metallic material is treated by the jellium model. Based on this method, we have studied the emitted x-ray spectra of Ar^{q+} hollow atoms and ions in the bulk of Ag as well as in the vacuum. By comparing the energy spectra of Ar^{q+} hollow atoms or ions in the vacuum and in the bulk of Ag, we can illustrate the conduction electron screening effect. Our calculated x-ray spectra of Ar^{q+} hollow atoms or ions in the bulk of Ag is in reasonable agreement with the experiment.

I. INTRODUCTION

The interaction of highly charged ions (HCI) with surfaces is a subject of increasing interest.[1-3] Basically, three steps are involved in the interaction of HCI with surfaces: (1) the formation of hollow atoms or ions above surfaces; (2) the decay of hollow atoms or ions at or below surfaces and (3) total neutralization of hollow atoms or ions in the bulk of materials.[1] The formation of hollow atoms or ions is strongly related to the HCI's impact velocity, incident angle and other dynamic parameters.[4] In the final neutralization step, hollow atoms or ions emit the Auger electrons[5,6] or x-rays.[7-9] The emitted x-ray can provide static information of hollow atoms or ions in the bulk of materials from the energy position and the dynamic information from the spectral intensity. Usually, the Hartree-Fock method is used to study the energy structure of hollow atoms or ions in a vacuum,[10,11] which can not provide the detailed information of hollow atoms or ions in the bulk of materials. The conduction electron screening effect was first studied by Zaremba et al.[12] by use of the density functional theory. Recently, Arnau et al.[13] have used the local density functional theory to study the energy structure of hollow atoms and ions in the bulk of metallic materials. The advantage of this method is that the total energy of the N-electron system is a function of the total electron density. Similar to the traditional local density functional theory,[14] such a method contains a spurious self-interaction energy, which should be removed in the exact calculation. To remove the self-interaction energy, we use the local spin density approximation with an optimized effective potential and self interaction correction (LSDA/OEP-SIC) method.[15-17] Such a method has been successfully applied to study the atomic energy structure both in the non-relativistic[16] and relativistic[18] cases. Different from atoms or ions in a vacuum, hollow atoms or ions in the bulk of metallic materials interact with free electrons in the conduction band as well. The conduction electron is treated by the jellium model at present. The advantages of our method are: 1) we use local *spin*-density approximation, which allows us to study the spin polarized hollow atoms or ions in the bulk of metallic materials; (2) we use the optimized effective potential with self-interaction correction for bound electrons, which can completely remove the self-interaction energy for bound electrons.

Based on this method, we have studied the energy structure of N^{q+} ions in the bulk of Al.[19] Now, we will study the energy structure of Ar^{q+} ions in the bulk of Ag, the emitted x-ray energy from $K^1L^yM^x$ to $K^2L^{y-1}M^x$ configurations and so on. We will give a brief description of our theoretical method in Sec. II and present our results and discussion in Sec. III.

II. THEORETICAL METHOD

The energy structure of conduction electrons in a metal-

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lic ma te rial can be stud ied by the jellium model.[20] In the jellium model, the dis crete ion cores are re placed by a ho mo-ge neous pos i tive back ground with the charge den sity equal to the con duc tion elec tron den sity due to the neu tral iza tion re-quire ment. For a given elec tron den sity ρ, an ef fec tive ra dial $r_s = (3/(4\pi\rho))^{1/3}$ is de fined and the con duc tion elec trons are filled up to the Fermi en ergy $\varepsilon_F = \frac{1}{2r_s^2}(9\pi/4)^{2/3}$. Based on the den sity func tional the ory with the op ti mized ef fec tive po ten-tial and self-interaction cor rec tion,[16] the to tal en ergy of a hol-low atom or ion in the bulk of me tal lic ma te ri als (the jellium model) can be ex pressed as:

$$E[\rho] = T_s[\rho] + E_{xc}[\rho_\uparrow, \rho_\downarrow] + V_{ext}[\rho] + J_A[\rho] + E^{SIC}[\rho_b] - T_s[\rho_o] - E_{xc}[\rho_{o\uparrow}, \rho_{o\downarrow}] - V_{ext}[\rho_o], \quad (1)$$

with

$$V_{ext}[\rho] = -\int \frac{Z}{r}\rho(\mathbf{r})d\mathbf{r},$$

$$J[\rho] = \frac{1}{2}\int \frac{\rho(\mathbf{r}')\rho(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'d\mathbf{r} - \int \frac{\rho(\mathbf{r}')\rho_o}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'d\mathbf{r} + \frac{1}{2}\int \frac{\rho_o\rho_o}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'d\mathbf{r},$$

$$\rho(\mathbf{r}) = \sum_\sigma (\rho_{b\sigma}(\mathbf{r}) + \rho_{o\sigma} + \delta\rho_{c\sigma}(\mathbf{r})) = \rho_b(\mathbf{r}) + \rho_o + \delta\rho_c(\mathbf{r}).$$

Here, $T_s[\rho]$ is the non-interacting elec tron ki netic en ergy, $E_{xc}[\rho]$, the ex change-correlation en ergy, $E^{SIC}[\rho_b]$, the self-interaction cor rec tion for bound elec trons and σ, the spin in-dex (spin-up and spin-down states). ρ_0 is the back ground con-duc tion elec tron den sity, ρ_b, the bound elec tron den sity and $\delta\rho_c$, the con duc tion elec tron den sity changes due to the in tro-duc tion of the hol low atom or ion. The back ground en ergy with out the hol low atom or ion is sub tracted in Eq. (1). The elec tron wave func tions can be ob tained by solv ing the fol-low ing Schrödinger equa tion as

$$\left[-\frac{\nabla^2}{2} + V_\sigma^{OEP}(\mathbf{r})\right]\psi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma}\psi_{i\sigma}(\mathbf{r}), \quad (2)$$

with

$$V_\sigma^{OEP}(\mathbf{r}) = \int \frac{\rho_b(\mathbf{r}') + \delta\rho_c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{\delta E_{xc}[\rho_\uparrow \cdot \rho_\downarrow]}{\delta\rho_\sigma} + V_\sigma^{SIC}(\mathbf{r}) - \frac{Z}{r} + V_{const},$$

$$\rho_{b\sigma}(\mathbf{r}) = \sum_b \psi_{b\sigma}^*(\mathbf{r})\psi_{b\sigma}(\mathbf{r}),$$

$$\delta\rho_{c\sigma}(\mathbf{r}) = \sum_l \int_0^{k_f} \psi_{l\sigma}^*(r, k)\psi_{l\sigma}(r, k)dk - \rho_{o\sigma}. \quad (3)$$

Note that $r\phi_{l\sigma}(r, k) \rightarrow \sqrt{2/\pi}\,sin(kr - l\pi/2 + 2\pi\delta_l)$ when $r \rightarrow \infty$, here δ_l is the phase shift and k_f, the elec tron mo men tum at the Fermi en ergy.

The bot tom of the Fermi en ergy is cho sen as zero of the en ergy. Eqs. (2) and (3) can be solved self-consistently. Since both the bond and con tin uum states are in volved in Eq. (2), we use a non-equal space ra dial grid in the in ner re gion and an equal space ra dial grid in the outer re gion. The ad van tage of the grid struc ture is that we can de scribe both the bound and con tin uum states accurately with lim ited com pu ta tional ef fort. With the con verged ef fec tive po ten tial in Eq. (3), we can ob tain the elec tron spin-density dis tri bu tion, to tal en ergy and phase shift for each par tial wave and so on.

From the the o ret i cal point of view, the im prove ments of the pres ent method[19] over the pre vi ous one[13] are: (1) we use the lo cal spin-density func tional ap prox i ma tion, which al-lows us to study the spin-polarized hol low at oms or ions in the bulk of metallic materials; (2) we include explicitly self-interaction cor rec tion for bound elec trons, which can give a better or bital en ergy and to tal en ergy.[16,18,19]

III. RE SULTS AND DIS CUS SION

Based on the LSDA/OEP-SIC method, we have cal cu-lated the en ergy struc ture of Ar^{q+} ions in the bulk of Ag. In the calculation, the conduction electrons are treated by the jellium model with $r_s = 1.60$. Al though the en ergy struc ture of Ar^{q+} hol low at oms or ions is la beled by $K^nL^yM^x$ fol lowed by the con ven tion in Ref. 13, it still has many con fig u ra tions within each con fig u ra tion. We listed all the L^y configurations used in the cal cu la tion in Ta ble 1. In prac tice, we cal cu lated the to tal en ergy for all pos si ble spin com bi na tions within each L^y con fig u ra tion listed in Ta ble 1. For the M^x con fig u ra-tions, we fill the M-shell from 3*s* first and then 3*p* se quen-tially for sim plic ity. With such con fig u ra tions, we cal cu lated the to tal en er gies of tran si tion up per and lower states (with 1 *s*

Table 1. The Configurations Used in the Calculation

L^1	L^2	L^3	L^4
$2p^1$	$2s^12p^1$ $2p^2$	$2s^22p^1$ $2s^12p^2$ $2p^3$	$2s^22p^2$ $2s^12p^3$ $2p^4$
L^5	L^6	L^7	L^8
$2s^22p^3$ $2s^12p^4$ $2s^12p^5$	$2s^22p^4$ $2s^12p^5$ $2p^6$	$2s^22p^5$ $2s^12p^6$	$2s^22p^6$

va cancy filled by a 2*p* elec tron in the up per state), emit ted x-ray en ergy, screen ing ef fect and phase shift. We will discuss each in de tail.

A. Total energies of Ar^{q+} ions in the bulk of Ag and in the vacuum

We have per formed the to tal en ergy cal cu la tions for Ar^{q+} ions in the vac uum and in the bulk of Ag by LSDA/OEP- SIC method. To com pare the two cal cu la tions of Ar^{q+} ions in the vac uum and in the bulk of Ag, we can il lus trate the screen ing ef fect of con duc tion elec trons. Fig. 1 shows the total en er gies of Ar^{q+} ions in the vac uum as well as in the bulk of Ag. Gen erally speak ing, the to tal en ergy de creases as the num ber of bound elec trons in creases. For Ar^{q+} ions in the bulk of Ag, the changes of the to tal en ergy with the num ber of elec trons in the M-shell are very smooth. For Ar^{q+} ions in the vac uum, such changes are much rapid than that of Ar^{q+} ions in the bulk of Ag. Such ob ser va tion can be un der stood as: when we add one more elec tron into the sys tem in the vac uum, the to tal en ergy will de crease rap idly. For Ar^{q+} ions in the bulk of Ag, due to the neu tral iza tion re quire ment, if we add one more elec tron, the less ef fect nu cleus charge will at tract less conduc tion elec trons, the to tal en ergy changes a lit tle due to the fact the net charge change around the nu cleus is al most zero.

Also we can see that add ing one more elec tron into the L-shell will re lease more en er gies than add ing one more electron into the M-shell as shown in Fig. 1. The en ergy dif ference for a given hol low atom or ion in the vac uum and the bulk of ma te rial will be re leased when the hol low atom or ion ap proaches to the sur face.

The to tal en ergy of Ar^{q+} ions in the bulk of Ag shows a dra matic change for some given con fig u ra tions as shown in Fig. 1. This is due to the fact that the short-range po ten tial changes dra mat i cally when one elec tron is added or re moved from that configuration. Detailed discussion will be presented in the dis cus sion of phase shifts.

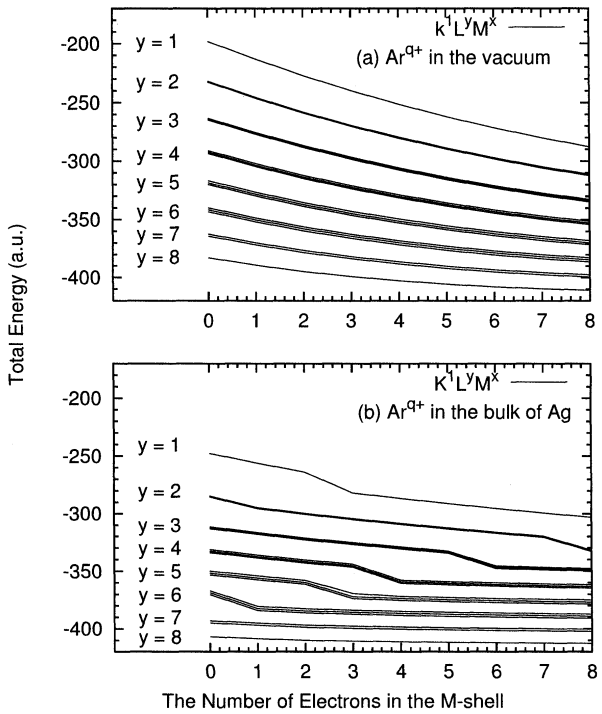

Fig. 1. The to tal en er gies of Ar^{q+} ions in (a) the vacuum and (b) the bulk of Ag.

B. X-ray spectrum of Ar^{q+} ions in the bulk of Ag

With the cal cu lated to tal en ergy, we can ob tain the x-ray tran si tion en ergy as

$$h\nu = E_{total}[K^1L^yM^x] - E_{total}[K^2L^{y-1}M^x] \quad (4)$$

for a given con fig u ra tion. The cal cu lated en er gies are shown in Fig. 2(a) by the solid ver ti cal line. To clearly see the shell struc ture, we off set one for each band (with the same num ber of elec trons in the L-shell). We also show the cor re spon dence value of Ar^{q+} ions in the vac uum by the dashed ver ti cal line.

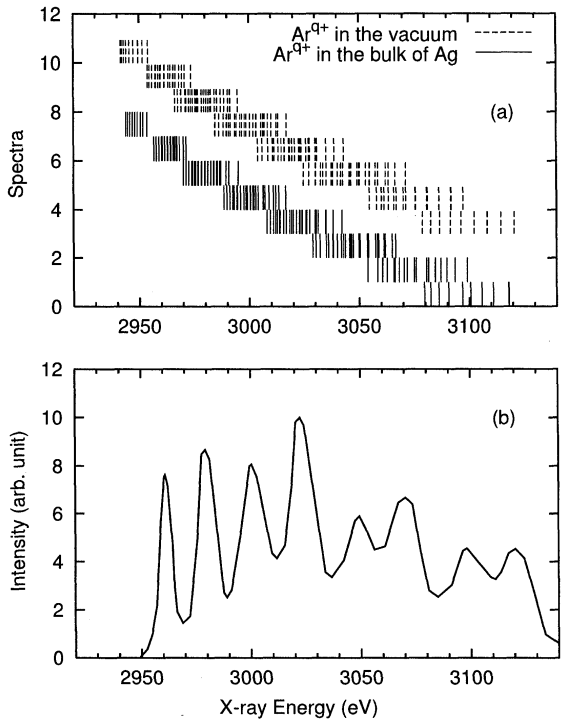

Fig. 2. (a) The cal cu lated x-ray en er gies of Ar^{q+} ions in the bulk of Ag (solid line) and in the vacuum (dashed line), and (b) the ex per i men tal x-ray spec tra.[7]

Note that the dashed line is offset by 4. For the spectra of Ar^{q+} ions in the vacuum, the energy levels are overlapped for different bands due to the filling of the M-shell. Thus, we can roughly claim that spectra in some energy region corresponds to the contribution for a given configuration, but not definitely. The experimental spectra can be expressed as

$$I(E) \propto \sum_i P(i) R_r(i) e^{-(E-E_r(i))^2/2\tau^2}, \quad (5)$$

with $P(i)$, the percentage of a given hollow atom or ion formed in the bulk of materials, $R_r(i)$, radiative decay rate of the hollow atom or ion, $E_r(i)$, transition energy of radiative decay and τ, energy resolution in the experiments. Here we use the gaussian line profile. In Eq. (5), to reproduce the experiment spectrum, we need static information ($R_r(i)$, $E_r(i)$) and dynamic information $P(i)$ and experiment energy resolution τ. In turn, if we know the experimental spectrum, we can abstract the dynamic information based on the calculated static properties ($R_r(i)$, $E_r(i)$).

For Ar^{q+} ions in the bulk of Ag, the spectra for given L^y fold is narrower than that in the vacuum, and the spectra for L^8 is clearly separated from other folds. This is due to the conduction electron screening effect, the same as we discussed above. The experimental spectra[7] are also shown in Fig. 2(b). By comparing with our calculated spectra, we can roughly assign each peak. The detailed assignment is still impossible since we do not know the dynamical information involved in the experiment. To compare with the experiment spectra, we need the percentage of each hollow atom or ion for a given configuration, which is strongly dependent on the experiment conditions, namely, the HCI's velocity, incident angle and so on. But our structure calculation can still provide some physical information and can help the experimenter to identify the spectra.

C. Density changes of conduction electrons

Based on the jellium model, the conduction electrons are homogeneous distributed over the whole bulk. With the introducing of Ar^{q+} ions into the material, the homogeneous electron gas will be perturbed and the density change is defined as

$$\delta\rho_c(r) = \rho_c(r) - \rho_o. \quad (6)$$

Since induced potential by Ar^{q+} ions is of a spherical symmetry, the density change is also of a spherical symmetry; here, we only show the radial density changes. Fig. 3 shows the conduction electron density changes with the perturbation of Ar^{q+} ions for $K^1L^1M^0$, $K^1L^1M^8$, $K^1L^8M^0$ and $K^1L^8M^8$ configurations, respectively, and the correspondence transition lower states. The four cases represent the situations of Ar^{q+} ions with almost empty L and M-shell electrons and full filled L and M-shell electrons. With the less bound electrons ($K^1L^1M^0$), more conduction electrons are attracted to the nucleus, which provide a screening field for the outer electrons. With most bound electrons ($K^1L^8M^8$), a few conduction electrons are attracted to the nucleus. For $K^1L^1M^8$, due to the full-filled M-shell electrons, the free electron is difficult to penetrate into the inner region. The total bound electron of $K^1L^8M^0$ is almost the same as $K^1L^1M^8$, but inner-shell full-filled, the perturbed electrons are concentrated relatively close to the nucleus. It is also true for the transition lower states, as shown in Fig. 3(b). Since the conduction electron density changes strongly relate to the phase shift, we will discuss the phase shift in detail.

D. Phase shifts

Fig. 4 shows the calculated phase shifts for the *s*, *p*, *d* and *f* partial waves in four electron configurations. Based on the Levinson theorem,[21] we conclude that 3 bound states (1*s*, 2*s*, 3*s*) exist for the *s* partial wave with the full filled L shell configurations $K^1L^8M^0$, $K^1L^8M^8$, and one more *s* bound state appears for $K^1L^1M^8$ and two more *s* bound states appear for $K^1L^1M^0$. In the vacuum, the number of bound states is infinite,

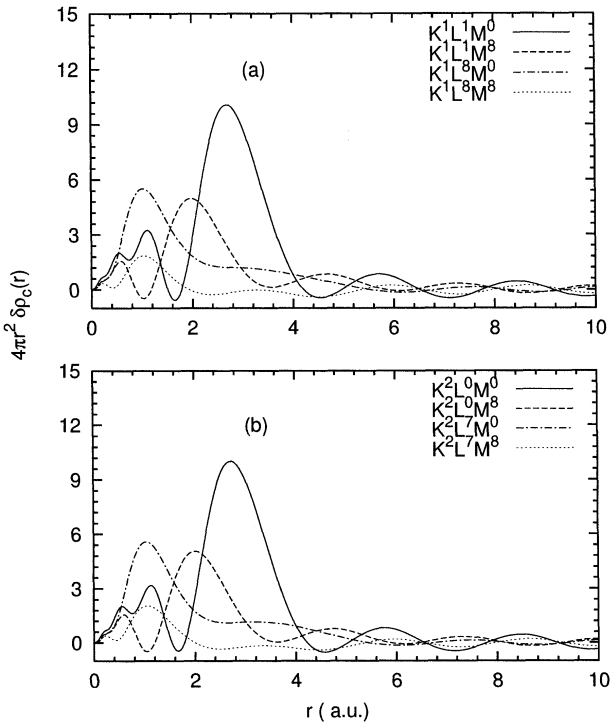

Fig. 3. Conduction electron density changes for the transition (a) initial and (b) final states.

which is different from the case in the bulk of metallic materials. Such things also appear in the *p*, *d* and *f* partial waves as shown in Fig. 4. Apart from the *p*-partial wave in the $K^1L^1M^0$ configuration, all the phase shifts of the *s* and *p* partial waves decrease monotonically as the energy increases. The phase shifts of the *d* and *f* partial waves increase as the energy increases. For $K^1L^1M^0$ configuration, the phase shift of the *p* partial wave increases first, then decreases as the energy increases. From the Friedel sum rule,[22]

$$N_c = Z - N_b = \sum_{l\sigma} (2l+1)(\delta_{l\sigma}(\varepsilon_F) - \delta_{l\sigma}(0)), \qquad (7)$$

with Z as the atomic number, N_b, the number of bound electrons in the hollow atom or ion, we can see that the screening electron comes from the *d* and *f* partial waves. Note that we have checked the total number of electrons within r_{max} sphere, which is in good agreement with Z. The calculated phase shifts are also very important for studying the stopping power of the low energy HCI moving in the bulk of metallic materials.[23-25]

To summarize, we have studied the energy structure of highly charged ions in the bulk of metallic materials by use of the LSDA/OEP-SIC method. The improvements over the existing local density functional method are: (1) we include the local spin-density functional method which allowed us to study the spin-polarized hollow atom or ion in the bulk of metallic materials; (2) we include the self-interaction correction for bound electrons, which can remove the self-interaction explicitly. Our calculated results are in reasonable agreement with the experiment.[7]

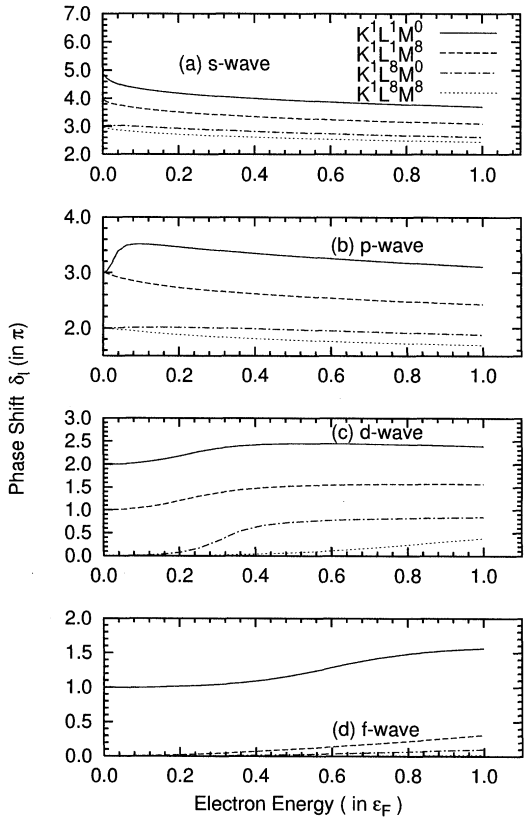

Fig. 4. Phase shifts of Ar^{q+} ions in the bulk of Al for (a) *s*, (b) *p*, (c) *d* and (d) *f* partial waves, respectively.

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Key Words

Hollow atoms; Energy structure; X-ray; Auger electron.

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