The Effect of Choice of Wave Functions on the Binding-Energy Increase in Ion-Atom Collisions

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The effect of the binding-energy increase during ion-atom collisions is estimated for K- and L-shell electrons by the use of the Hartree-Fock wave functions. The calculated results are compared with those obtained from the hydrogenic wave functions. The effect of choice of wave functions for the binding-energy increase on the K- and L-shell ionization cross sections by charged-particle impact is discussed.

KEY WORDS: Ion-atom collision/ Binding-energy increase/ Hartree-Fock wave function/

I. INTRODUCTION

In the course of ion-atom collisions, the binding energy of the inner-shell electrons in the target atom increases due to penetration of the projectile into the field of the target atom. This effect, called the binding-energy effect, plays an important role and reduces the ionization cross sections for low-energy projectiles. Basbas *et al.*[1] estimated the binding-energy increase for K-shell electron in the perturbed-stationary-state theory. Their result was incorporated into the plane-wave Born-approximation (PWBA) formula for the K-shell ionization cross section together with the Coulomb-deflection effect of the projectile (CPSS). Brandt and Lapicki[2] extended this model to the case of L-shell ionization. In the CPSS theory, the binding-energy increase is estimated by the use of the nonrelativistic screened hydrogenic (SH) wave functions.

When the atomic number of the target is high, the electronic relativistic effect on the binding-energy increase becomes important. The estimation of such an effect has been made by using the relativistic hydrogenic (Dirac) wave functions for K-shell[3,4] and L-shell electrons.[5,6] It is found that the relativistic wave functions give considerably larger binding-energy increase than the nonrelativistic ones.

On the other hand, for target elements with low atomic numbers the SH model is not good approximation to the atomic electrons and more realistic wave functions, such as Hartree-Fock (HF) wave functions, should be used. In this case, the deviation of the shape of the SH wave functions from that of the HF wave functions may affect on the binding-energy increase. This effect is expected to be larger for L shell than for K shell, because the L-shell electrons are shielded by the K-shell electrons. It is the purpose of the present paper to estimate the effect of choice of the wave functions

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on the binding-energy increase of K- and L-shell electrons during ion-atom collisions and its influence on the ionization cross section by charged-particle impact.

II. INCREASE IN BINDING ENERGY

In the first-order perturbation theory, the change in the binding energy of the s-shell electron due to presence of the projectile is given by:[1]

$$\Delta E_s = \int \psi_s{}^*(\boldsymbol{r}) \frac{Z_1 e^2}{|\boldsymbol{R}-\boldsymbol{r}|} \psi_s(\boldsymbol{r}) d\boldsymbol{r}, \tag{1}$$

where $\psi_s(\boldsymbol{r})$ is the unperturbed wave function for the s-shell electron, Z_1 is the projectile charge, $\boldsymbol{R}$ is the coordinate of the projectile, and $\boldsymbol{r}$ is that of the s-shell electron.

For the atomic wave function, we use the Hartree-Fock wave function in the Roothaan form.[7] In this model, the self-consistent-field wave function is expressed in terms of basis functions

$$\psi_{i\lambda\alpha}(\boldsymbol{r}) = \sum_p \chi_{p\lambda\alpha}(r, \theta, \phi) C_{i\lambda p}, \tag{2}$$

where a subscript λ indicates the symmetry species, α represents the subspecies belonging to λ, i labels the i-th orbital of symmetry λ, and p refers to the p-th basis function of symmetry λ. The expansion coefficient $C_{i\lambda p}$ depends on i, λ, and p, but is independent of the subspecies α. The basis functions χ are chosen to be Slater-type orbitals with integer quantum numbers:

$$\chi_{p\lambda\alpha}(r, \theta, \phi) = R_{\lambda p}(r) Y_{\lambda\alpha}(\theta, \phi), \tag{3}$$

where

$$R_{\lambda p}(r) = N_{\lambda p} r^{n_{\lambda p}-1} \exp(-\zeta_{\lambda p} r), \tag{4}$$

$$N_{\lambda p} = [(2n_{\lambda p})!]^{-1/2} (2\zeta_{\lambda p})^{n_{\lambda p}+1/2}, \tag{5}$$

and $Y_{\lambda\alpha}(\theta, \phi)$ is the normalized spherical harmonics. The principal quantum number $n_{\lambda p}$ is chosen to be $n_{\lambda p} \geq \lambda+1$, and the exponent $\zeta_{\lambda p}$ is determined so as to give the best energy eigenvalue by the optimization techinique. The values of $C_{i\lambda p}$ and $\zeta_{\lambda p}$ are given in the table prepared by Clementi and Roetti.[8] The wave functions for L_2 and L_3 shells are produced as appropriate linear combinations of Eq. (2) in the L-S coupling scheme.

Using the multipole expansion of $1/|\boldsymbol{R}-\boldsymbol{r}|$, we can easily perform integration over angular vaiables. After averaging over initial electron states, we obtain the universal expression for K and L shells:

$$\Delta E_s = Z_1 e^2 \sum_{p, p'} C_{i\lambda p} C_{i\lambda p'} \left\{ \frac{1}{R} \int_0^R R_{\lambda p}(r) R_{\lambda p'}(r) r^2 dr + \int_R^\infty R_{\lambda p}(r) R_{\lambda p'}(r) r dr \right\}, \tag{6}$$

where $R = |\boldsymbol{R}|$.

Following the method of Basbas et al.,[1] we assume that the projectile is described classically by a straight-line trajectory with an impact parameter b and that R can be approximately set to be equal to b. Then the radial integration in Eq. (16) can be performed analytically and we obtain the scaled binding-energy increase in units of Rydberg as a function of b:

$$\frac{\Delta E_s}{Z_1 Z_{2s}} = \frac{2}{Z_{2s}} \sum_{p, p'} C_{i\lambda p} C_{i\lambda p'} N_{\lambda p} N_{\lambda p'} \frac{1}{a^n t} \times \{\gamma(n+1, t) + t\Gamma(n, t)\}, \tag{7}$$

where $n = n_{\lambda p} + n_{\lambda p'}$, $t = ab$, and $a = \zeta_{\lambda p} + \zeta_{\lambda p'}$.

The effective nuclear charge Z_{2s} is taken to be $Z_{2K} = Z_2 - 0.3$ for K shell and

$Z_{2L} = Z_2 - 4.15$ for L shell, where Z_2 is the atomic number of the target element. The function $\gamma(a, x)$ and $\Gamma(a, x)$ are the incomplete gamma function of the first and second kind, respectively.[9]

Since n is integer in the present case, the incomplete gamma functions can be written in terms of the product of exponential function and power series.[9] Thus we finally obtain

$$\frac{\Delta E_s}{Z_1 Z_{2s}} = \frac{2}{Z_{2s}} \sum_{p,p'} C_{i\lambda p} C_{i\lambda p'} N_{\lambda p} N_{\lambda p'} \frac{n!}{a^n t}$$
$$\times \left\{ 1 - \exp(-t) \left[\frac{1}{n} \sum_{r=1}^{n-1} \frac{r}{(n-r)!} t^{n-r} + 1 \right] \right\}. \tag{8}$$

This equation gives the scaled binding-energy as a function of the impact parameter b. In the limit of $b \to 0$, Eq. (8) reduces to

$$\frac{\Delta E_s}{Z_1 Z_{2s}} = \frac{2}{Z_{2s}} \sum_{p,p'} C_{i\lambda p} C_{i\lambda p'} N_{\lambda p} N_{\lambda p'} \frac{(n-1)!}{a^n}. \tag{9}$$

III. RESULTS AND DISCUSSION

In Fig. 1, the scaled binding-energy increase for K shell, $\Delta E_K / Z_1 Z_{2K}$, is plotted as a function of impact parameter for aluminum $(Z_2 = 13)$, copper $(Z_2 = 29)$, and silver $(Z_2 = 47)$. The binding-energy increase is given in units of Rydberg and the impact parameter is measured in the K-shell radius $a_{2K} = a_0/Z_{2K}$, where a_0 is the first Bohr radius. For comparison, the values obtained from the SH model are also plotted in the figure.
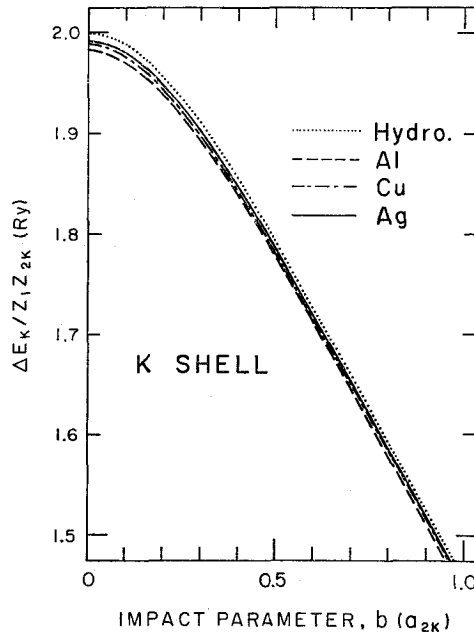

Fig. 1. The increase in scaled binding energy of K shell, $\Delta E_K / Z_1 Z_{2K}$, as a function of impact parameter for aluminum, copper, and silver. The dotted line represents the results by the screened hydrogenic wave function.

For the SH wave functions, $\Delta E_K/Z_1 Z_{2K}$ has a universal property and is independent of Z_2. However, this quantity is a function of Z_2 in the case of the HF wave functions. It is clear from the figure that the hydrogenic wave functions overestimate the binding-energy increase in the K-shell electron for low-Z_2 elements. For high-Z_2 elements, the HF curve approaches to the SH one. The difference between the HF and SH values is larger for small impact parameters and maximum at $b=0$. For large impact parameters, the scaled binding-energy increase for the HF wave functions approaches to the hydrogenic value for all elements.
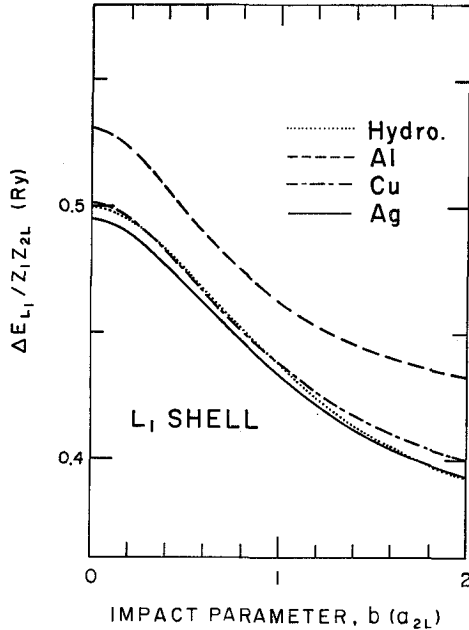
Fig. 2. The increase in scaled binding energy of L_1 shell, $\Delta E_{L1}/Z_1 Z_{2L}$, as a function of impact parameter for aluminum, copper, and silver. The dotted line represents the results by the screened hydrogenic wave function.

Fig. 3. The increase in scaled binding energy of $L_{2,3}$ shell, $\Delta E_{L2,3}/Z_1 Z_{2L}$, as a function of impact parameter for aluminum, copper, and silver. The dotted line represents the results by the screened hydrogenic wave function.
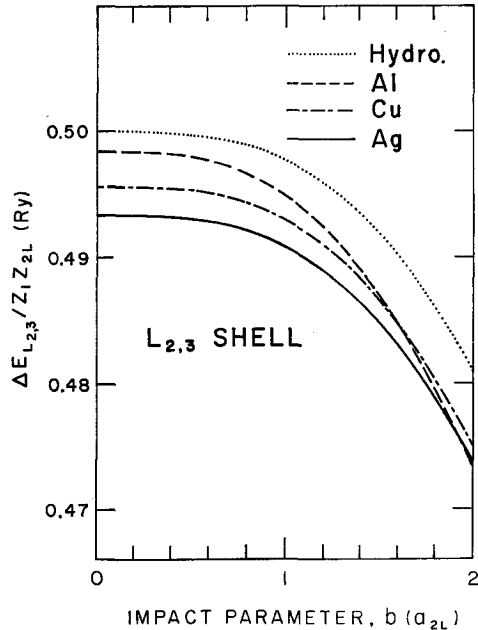
Figure 2 shows the scaled binding-energy increase for L_1-shell electron of aluminum $(Z_2=13)$, copper $(Z_2=29)$, and silver $(Z_2=47)$ as a function of impact parameter. The energy is expressed in units of Rydberg and the impact parameter is measured in units of $a_{2L}=a_0/Z_{2L}$. In this case, the SH wave functions give smaller binding-energy increase for light elements, but larger value for medium elements.

Similar plot for $L_{2,3}$-shell electron is shown in Fig. 3 and compared with the SH values. For small impact parameters, the SH model overestimates the binding-energy increase. The discrepancy between the SH and the HF values becomes larger with increasing Z_2.

In order to estimate the effect of change in the binding-energy increase on the total s-shell ionization cross sections, the ΔE_s values obtained above should be averaged

over impact parameters by the use of the impact-parameter-dependent s-shell ionization cross sections and incorporated into the CPSS theory. This can be done through the binding-energy factor defined by[1,2]

$$\varepsilon_s = 1 + \langle \Delta E_s \rangle / E_s, \tag{10}$$

where E_s is the s-shell binding energy of the ordinary atom and $\langle \Delta E_s \rangle$ is the average increase in the s-shell binding energy during ion-atom collision.

The average value of ΔE_s is obtained from

$$\langle \Delta E_s \rangle = \int_0^\infty \Delta E_s(x) W_s(x) x \, dx, \tag{11}$$

where $x = bq_0$, q_0 is the minimum momentum transfer to an s-shell electron, and $W_s(x)$ is the weighting function determined from the s-shell ionization cross section with the impact parameter b. According to Brandt and Lapicki,[2] the normalized weighting functions are

$$W_{K, L_1}(x) = \frac{5}{32} x^4 K_2^2(x), \tag{12}$$

for K and L_1 shells, and

$$W_{L_{2,3}}(x) = \frac{1}{192} x^6 [K_2^2(x) + K_3^2(x)], \tag{13}$$

for L_2 and L_3 shells,[10] where $K_l(x)$ is the modified Bessel function of the second kind.

Using the binding-energy factor ε_s thus obtained, the binding energy of the target electron E_s is replaced by $\varepsilon_s E_s$ in the CPSS theory corrected for relativistic effect (CPSSR).[11] The calculations of the ionization cross sections have been made by the use of the computer code DEKY2.[12] The calculated results show that the binding-energy effect evaluated by Eq. (8) increases the K-shell ionization cross section for 100-keV protons by 1% for Al, 0.5% for Cu, and 0.4% for Ag, respectively. In the case of 1.5-MeV ^{16}O-ion bombardments, the increase in the K-shell ionization cross sections is 5% for Al, 3% for Cu, and 2% for Ag. The effect is larger for higher-Z_1 projectiles and for lower-Z_2 target elements.

For L_1-shell ionization cross sections by 100-keV proton impact, the use of the HF wave functions in the binding-energy effect decreases the SH values by 2.7% for Al and 0.5% for Cu, but gives rise to increase by 3% for Ag. On the other hand, the L_2- and L_3-shell ionization cross sections increase by about 1% for these three elements. Similar calculations for 1-MeV ^{16}O-ions show that the L_1-shell cross section decreases by 10.5% for Al and 4.5% for Cu, and increases by 3.4% for Ag. The L_2- and L_3-shell ionization cross sections increase by about 7% for all these elements.

IV. CONCLUSION

The binding-energy increase during ion-atom collision has been estimated for K- and L-shell electrons by the use of Hartree-Fock wave functions. The increase in the scaled binding energy thus obtained for low- and medium-Z_2 elements is compared with the value obtained by the screened hydrogenic wave functions. It is found that the screened hydrogenic wave functions overestimate the binding-energy increase for K- and $L_{2,3}$-shell electrons. On the other hand, for L_1-shell the screened

hydrogenic values are smaller for low-Z_2 elements and higher for medium-Z_2 targets.

These results have been incorporated in the CPSSR theory and the K- and L-shell ionization cross sections have been calculated. For the total K- and L-shell ionization cross sections, the effect of choice of wave functions for the binding-energy increase is not so large, at most 10%, and in most cases may be comparable to or within the errors of the CPSSR calculations. However, it should be noted that in the present CPSSR theory all the calculations, except for the binding-energy increase, are made by using the hydrogenic wave functions. Especially for small impact parameters, the impact-parameter-dependence of the K- and L-shell ionization cross sections with Hartree-Fock wave functions would be different from that with the hydrogenic wave functions.

It is hoped to perform the calculations for the K- and L-shell ionization cross sections with Hartree-Fock wave functions, using the present results for the binding-energy effect.

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