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Molecular-orbital model for slow hollow atoms colliding with atoms in a solid

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A model that has previously been used to calculate the molecular orbitals in atomic collisions between neutral atoms and ions is extended to describe hollow atoms colliding with a solid. The energy levels and screening functions are obtained from density-functional calculations. The results show that the inner-shell holes in the hollow projectile, as well as the screening cloud within the solid, create important effects that are essential for the description of the interaction of multicharged ions with solids.

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The interaction of slow, highly charged ions with surfaces has received a great deal of attention in the past few years [1–15]. Information about the interaction can be obtained by measuring the spectra of emitted photons and electrons, sputtered ions, and the energy loss of the projectile ions. In particular, the low- and high-energy Auger electrons emitted contain information about the charge transfer between the ion and the solid. Since the early work of Arifov *et al.* [16], where the formation of a hollow atom by resonant electron capture into high Rydberg states was proposed, most of the theoretical work [17,18] has been concentrated on physical processes that take place as the ion approaches the solid surface. However, recent experiments [19] show that even for energies as low as a few hundred eV the ions penetrate into the first few layers of the solid, where the number of degrees of freedom is so large that very little understanding has been achieved up to now. For example, the way in which the Rydberg electrons in the hollow atom are perturbed, i.e., interact with target bound or continuum electrons and are eventually removed, is still a matter of controversy.

When a hydrogenlike ion of first row atoms moves into a metal a screening cloud of the size of the M shell is almost immediately formed around the ion, whereas its L shell remains empty for a finite time. In this way hollow atoms of the second generation are formed within shallow surface layers. The lifetime of these hollow atoms is still a subject of controversial discussion. Auger transitions are an efficient mechanism for the filling of the L shell. On the other hand, as the projectile approaches the target atoms the atomic energy levels couple and molecular orbitals are formed. Therefore further mechanisms, such as resonant electron capture at curve crossings, contribute to the L-shell filling [7]. Up to now little information has been available on the charge-transfer cross sections.

In the present work we study the formation of molecular orbitals from the atomic L-shell levels on hollow Ne atoms in the bulk of Al. The determination of the energy levels and screening functions needed in the calculation of the model matrix elements is our main motivation. Nonlinear screening effects in the metal and the presence of inner-shell holes are considered within the framework of density-functional theory. Total energies for each configuration are used to calculate the energy levels, and the screening charges are obtained by integration of the self-consistent charge densities. The results show that for the Ne+Al system L-shell vacancy transfer from the hollow Ne projectile to the target Al core occurs via two mechanisms: level crossings (Landau-Zener) and orbital promotion (Fano-Lichten).

We consider a slowly moving hollow atom in a metal ($v \ll v_F$, where v is the ion velocity and v_F is the Fermi velocity of the metal electrons) as a static point charge Z_1

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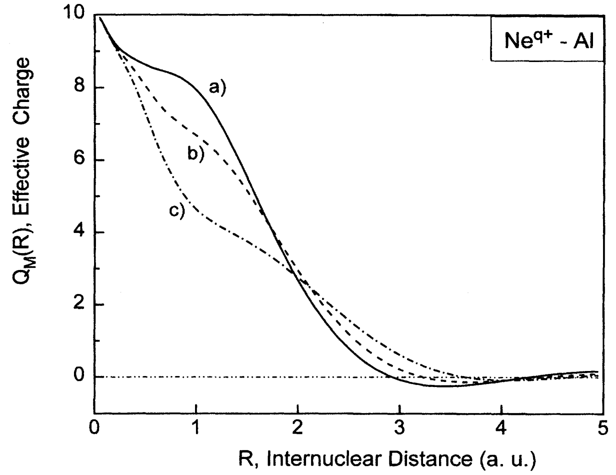

FIG. 1. Screening functions for Ne hollow atoms with different numbers of L-shell electrons. Curves (a), (b), and (c) correspond, respectively, to 0, 2, and 5 L-shell electrons.

surrounded by an appropriate electron cloud (with inner-shell holes) immersed in an electron gas. Furthermore, we assume that the metal electrons screen sufficiently rapidly within a time scale given by the inverse plasma frequency ($\omega_p \cong 10^{-16}$ sec). Due to the strength of the perturbation that a multicharged ion ($Z_1 \gg 1$) represents to the valence electrons, linear response theory is not expected to be valid [20]. Density-functional theory [21,22] allows us to treat the screening in a self-consistent way for arbitrary Z_1 value by solving the equations

$$\{-\tfrac{1}{2}\Delta + V_{\text{eff}}[\rho]\}\Phi_i = \varepsilon_i \Phi_i , \tag{1}$$

where $V_{\text{eff}} = V_{\text{ext}} + V_{\text{ind}} + V_{\text{xc}}$, with

$$V_{\text{ext}} = -\frac{Z_1}{r}, \quad V_{\text{ind}} = \int dr' \frac{\rho(r')}{|r-r'|}, \tag{2}$$

and $V_{\text{xc}}[\rho]$ is the exchange correlation potential in the local density-approximation (LDA) [23]. The density $\rho(r)$ appearing in Eq. (2) is obtained from the orbitals as

$$\rho = \sum_{i \in \text{occ}} |\Phi_i|^2, \tag{3}$$

where the sum includes both the sum over occupied discrete bound states and an integration over the continuum up to the Fermi level. For partially filled shells a spherical average is performed. This set of equations is solved self-consistently by iteration. In the case of hollow atoms the number of occupied bound states (n_{occ}) is lower than the total number of bound states (n_b), the difference being the number of holes (n_h). The generalization of the Friedel sum rule [24] that expresses the charge neutrality in the system by equating the amount of displaced charge to the impurity charge, is

$$Z_1 + n_h = \frac{2}{\pi} \sum_l (2l+1)\,\delta_l(k_F), \tag{4}$$

TABLE I. Ne($1s2l^nL$) energy levels (in a.u.) for different numbers of L-shell electrons.

n_L	$-\varepsilon_{2s}$	$-\varepsilon_{2p}$
1	5.34	4.88
2	5.02	4.48
3	4.59	4.00
4	4.14	3.48
5	3.70	2.97
6	3.33	2.50
7	2.83	2.05
8	2.43	1.63

where $\delta_l(k_F)$ is the l-partial wave phase shift at the Fermi level.

The screening function $Q_M(R)$ is given by

$$Q_M(R) = Z_1 - 4\pi \int_0^R du\, u^2 \delta\rho(u), \tag{5}$$

where $\delta\rho(r)$ is $\rho(r) - \rho_0$ and ρ_0 is the background electron density. In Fig. 1 we plot the screening functions for different electronic configurations of the hollow Ne atom. We see that as the number of L-shell holes increases there is not only a net increase of charge within the first two atomic units but also an overscreening at a distance of about 3 a.u. This reflects the tendency of the metal valence electrons to screen the large positive charge at the origin. Overscreening would not occur using linear response theory, where the amount of displaced charge is just proportional to the impurity charge.

The total energy for each configuration is obtained from

$$E[\rho] = T + E_{\text{es}} + E_{\text{xc}}, \tag{6}$$

where

$$T = \sum_{i \in \text{occ}} \varepsilon_i - \int dr' \rho(r') V_{\text{eff}}(r'), \tag{7}$$

$$E_{\text{es}} = \int dr' \rho(r') \left\{ V_{\text{ext}}(r') + \tfrac{1}{2} \int dr \frac{\rho(r)}{|r-r'|} \right\}, \tag{8}$$

$$E_{\text{xc}} = \int dr\, \rho(r) \varepsilon_{\text{xc}}[\rho(r)], \tag{9}$$

where $\varepsilon_{\text{xc}}[\rho]$ is the exchange and correlation energy density. T, E_{es}, and E_{xc} correspond to the kinetic, electrostatic, and exchange and correlation energy, respectively. We subtract the background values by taking into account that $\rho = \rho_0$ for $Z_1 = 0$ and that there is a background of positive charge keeping charge neutrality in the system. This means that $T[\rho_0]$ and $E_{\text{xc}}[\rho_0]$ are subtracted ($E_{\text{es}}[\rho_0] = 0$ because of charge neutrality). Then, we can use the total energy differences between two different electronic configurations to calculate the bound-state energy levels.

We have calculated the L-shell energy levels of Ne ions with several configurations with a different number of L-shell electrons, immersed in bulk Al metal. To calculate the L-shell energy levels and screening function of the Al atoms we use the vacancy in the jellium model [25] that

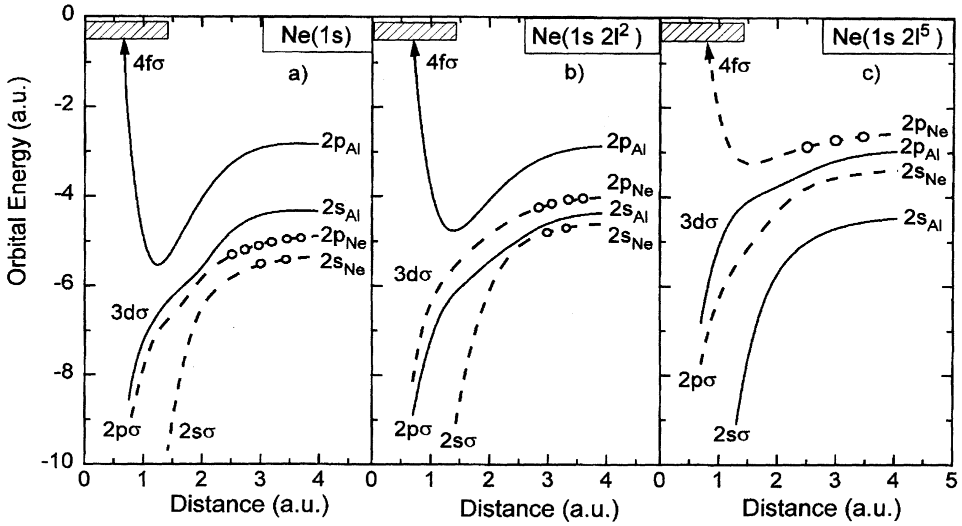

FIG. 2. Molecular-orbital energies evaluated by diagonalization of model matrix elements [27]. In (a), (b), and (c) the data for hollow Ne with 0, 2, and 5 electrons in the L shell are shown, respectively. The dots show the number of L-shell holes in the hollow Ne atoms for each configuration.

takes into account the fact that three electrons per Al atom (the valence electrons) are already contributing to the valence electron density. If we denote the total energy of a given electronic configuration by its occupation numbers, i.e., $E(n_{1s},n_{2s},n_{2p},\ldots)$, the L-shell energy levels are obtained from

$$\varepsilon_{2s}=E(n_{1s},n_{2s},n_{2p})-E(n_{1s},n_{2s}-1,\ n_{2p}), \quad (10)$$

$$\varepsilon_{2p}=E(n_{1s},n_{2s},n_{2p})-E(n_{1s},n_{2s},n_{2p}-1). \quad (11)$$

These values are close to the eigenvalues at half occupancy of the level (Slater rule). When comparing with atomic structure calculations we take into account that the vacuum level is above the bottom of the band (our zero of energy) by an amount $E_F+\phi$, where E_F is the Fermi energy and ϕ the metal work function.

To refer these energy levels to the vacuum we take into account the different origins of the energy scales:

$$\varepsilon_i^{\mathrm{vac}}=\varepsilon_i^{\mathrm{sol}}+E_F+\phi. \quad (12)$$

In Table I we show the average L-shell energy levels for Ne hollow atoms with a different number of L-shell electrons. These L-shell energy levels are close (within 0.3 a.u.) to those obtained from atomic code calculations [26] when the outer-shell screening is taken into account by filling the lowest-lying levels in the outer shell (M shell in our case) until charge neutrality is achieved [9,12]. Thus the valence electron screening in the solid is similar to that by the M-shell electrons in the atom. For the outer shells this is of course no longer valid since they may not even be bound. It should be added that for the L-shell Al levels we obtain $\varepsilon_{2s}=-4.4$ a.u. and $\varepsilon_{2p}=-2.9$ a.u.

The molecular-orbital (MO) calculations are based on matrix elements that have been evaluated previously within a screened hydrogenic model (SHM) by Stolterfoht [27]. They are given as a function of the internuclear distance R (in a.u.):

$$H_{ii}^{NN}=\varepsilon_i^0-\frac{1-e^{d\alpha_i R}}{R}\,Q_M(R), \quad (13)$$

$$H_{ij}^{NN}=-\frac{3}{2}\,\frac{1-P(d'\alpha_{ij}R)e^{-d'\alpha_{ij}R}}{\beta_{ij}R^2}\,Q_M(R), \quad (14)$$

$$H_{ij}^{NM}=k\beta_{ij}e^{-c\alpha_{ij}R}, \quad (15)$$

where i and j label the L-shell orbitals $2s$ and $2p$ centered at the collision partners labeled N and M. The polynomial $P(x)$ is given in Ref. [27]. Equation (13) represents the diagonal matrix elements, whereas Eqs. (14) and (15) describe the nondiagonal matrix elements of orbitals located at one center and two centers, respectively. As described in Ref. [27], the model matrix elements were simplified in replacing polynomials in front of exponential functions by dimensionless constants. On the other hand, the flexibility of the matrix elements was increased by introduction of further (dimensionless) constants. The constants were adjusted to fit molecular orbitals evaluated independently by means of a Hartree-Fock code [27]. The values of the constants are $c=0.86$, $d=0.5$, $d'=1.5$, and $k=3.6$. The variable quantities of the SHM matrix elements are the "velocity" parameters $\alpha_i=|2\varepsilon_i^0|^{1/2}$ deduced from the corresponding binding energies ε_i^0. These quantities were utilized to determine the mean values $\alpha_{ij}=(\alpha_i+\alpha_j)/2$ and $\beta_{ij}=(\alpha_i\alpha_j)^{1/2}$. The SHM model is originally developed to treat slow collisions between atoms and ions or atoms, and so describes reasonably well the physics (like the screening functions) in the interaction region ($1<R<3$ a.u., in our case). The simple exponential screening function $Z_M\exp(-\alpha_0 R)$ used for atom-

atom collisions can be generalized in the case of hollow atom-atom collisions to $(Z_M+n_h)\exp(-\alpha_0 R)$, where $\alpha_0=0.42(\alpha_{ij})^{2/3}$.

The model matrix elements for hollow Ne colliding with Al were used to evaluate the corresponding MO energies by means of numerical diagonalization [28]. The analysis was restricted to σ orbitals. Examples for the results of the MO energies are given in Fig. 2, which refers to Ne with different numbers of electrons in the L shell. Asymptotically, at large internuclear distances, the MO's correlate with the $2s$ and $2p$ level of Ne and Al. It is seen [in particular, from Fig. 2(a)] that the $4f\sigma$ orbital, correlated with the Al $2p$ level, decreases strongly in energy before it undergoes the typical promotion predicted by the Fano-Lichten model [29]. This energy decrease can be considered as a characteristic effect of the Ne hollow atom that is highly ionized in the L shell and, hence, strongly affects the collision partner Al at intermediate distances (see the corresponding screening function in Fig. 1).

A similar decrease also causes the approach of the $3d\sigma$ MO and the $2p\sigma$ MO, so that an avoided crossing appears at about 2.2 a.u. [Fig. 2(a)]. Here, couplings between the MO's occur where the transfer into the empty L shell of Ne may occur. For two electrons in the L shell a similar crossing occurs between the $2p\sigma$ and $2s\sigma$ MO's correlating with the Al $2s$ and Ne $2s$ levels, respectively [Fig. 2(b)]. As the number of L-shell electrons increases the levels of Ne are shifted beyond the Al $2p$ level. Then, the Ne $2p$ level correlates with the $4f\sigma$ MO, so that the remaining vacancies are likely to be promoted into the conduction band of Al [Fig. 2(c)].

In conclusion, we have found two characteristic features of the screening of hollow atoms in metals: (i) a strong positive charge within the first few atomic units (hollow character) and (ii) an overscreening at about the size of the hollow atom, i.e., the M-shell radius (nonlinear screening). For the Ne+Al system our results show that the L-shell vacancy transfer between the hollow Ne ion and the Al atomic levels may take place via level crossings (Landau-Zener mechanism) and level promotion (Fano-Lichten mechanism) as a consequence of the strong interaction in the region $1<R<3$ a.u. between molecular orbitals that correlate with the atomic L-shell levels of Ne and Al. These processes compete with Auger processes in the filling of the L shell. The calculation of the cross sections for these processes will be done in a future publication [30]. It will be interesting to obtain experimental data for targets with different electronic structures like carbon or LiF, where the lack of energy levels between the K shell and the valence band in the former and the presence of a large band gap in the latter may give rise to new effects. These studies are expected to assist in a better understanding of the L-shell filling of hollow atoms in solids.

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