

Model calculation of the charge transfer in low-energy He⁺ scattering from metallic surfaces

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Charge-transfer mechanisms in low-energy helium-scattering spectroscopy are analyzed by using an Anderson-like description of the time-dependent collisional process, which allows us to include several electronic bands of extended and localized nature in the solid. The Hamiltonian parameters are obtained from a Hartree-Fock self-consistent-field calculation of the He-target atom dimeric system. We examine in particular cases such as Ca and Ga linear chain substrates. We found that at velocities large enough, the localized state in the solid contributes to the He⁺ neutralization, showing the characteristic oscillatory behavior of the nonadiabatic charge exchange between localized states, in agreement with other calculations. In the range of low velocities we found that if the hybridization between the He orbital and the localized states in the solid is able to produce the formation of an antibonding state having a predominant weight of the He-1s orbital, this promotes the charge exchange between the Helium and the extended bandstates of the solid.

I. INTRODUCTION

Among the processes involving charge exchange in the inelastic scattering of atomic or ionic projectiles from metal surfaces, one can have neutralization due to Auger, resonant, and quasisonant charge-exchange processes. These are accompanied by small changes in the kinetic energy of the projectile while re-ionization, where an electron of a neutralized projectile is transferred to a vacant valence state of the surface, implies an energy loss comparable to the ionization energy of the projectile.

Experiments performed over a wide variety of samples have shown interesting trends in the charge-exchange probability as a function of the kinetic energy of the projectile concerning the nature of the target system. These have been related to the presence of localized *d*-like states in the valence-band structure or with corelike states of the substrate atoms. Erickson and Smith¹ studied the scattering of He⁺ by Bi, Pb, In, Ga, Ge, Sn, and Sb substrates and reported an oscillatory behavior of the backscattered ion intensity as a function of the primary ion energy. More recently, Souda *et al.*^{2,3} performed experiments for many substrates of pure elements and compounds. They found that reionization of He⁰ sometimes makes an important contribution to the He⁺ spectra at kinetic energies as low as and below 1 keV. This is thought to be produced by the promotion of one He 1s electron with a binding energy of 24.6 eV into a vacant level of the surface. The ratio between the He⁺ intensity produced by He⁰ incidence relative to that produced by He⁺ incidence, I^0/I^+ , is proposed as a measure of the promotion of the He 1s orbital.³ Experiments performed on the II-b group elements have shown that the values of I^0/I^+ exhibit a sharp decrease in these systems. Thus, for Zn or Cd, this ratio is about three orders of magnitude smaller than that for Ca.

Similar experimental results have been obtained by Mikhailov *et al.*⁴ The oscillatory intensities observed in ion-surface scattering are explained through a near-resonant charge exchange between the He 1s orbital and the energetically near-*d* orbitals of the surface atoms. By using a wavefunction formalism where the time evolution of the system is described in terms of localized and continuous states, Tully⁵ was able to account for an oscillatory behavior of the ionization probability as caused by the nonadiabatic charge transfer between the atom and localized state in the solid. Tsuneyuki and Tsukada⁶ have explained the re-ionization of neutralized helium as due to the crossings of the He 1s level with empty valence levels of the target. Their conclusions were obtained from an *ab initio* self-consistent Hartree-Fock (HF) calculation of the diatomic He-target-atom system. They estimated the threshold energies for re-ionization, finding good agreement with the measured values in some systems, but for other targets such as In and Sn they were unable to explain the experimental results.²

In this work we analyze the charge-exchange probability for scattering of He⁰ and He⁺ from metallic surfaces by using a time-dependent quantum formalism which allows to incorporate several electronic bands of localized and extended nature for the substrate.⁷ The parameters of the interaction Hamiltonian are obtained from an *ab initio* model based on a superposition of pair bonds,^{8,9} which accounts for a realistic description of each dimeric system. We examine the role played by the presence of narrow *d* bands or corelike states of the solid on the charge-exchange process for different substrates. We have selected metallic Ga and Ca substrates because they involve the kinds of localized states in the solid we want to study and also because it was found that, while in the Ca case the re-ionization is very important-

t, in the Ga case this is negligible.^{2,3}

This paper is organized as follows: In Sec. II a brief description of the theory is given, and Sec. III is devoted to

present the model system, while in Sec. IV the results of our calculation are analyzed and discussed. Finally, a summary is presented in Sec. V.

II. THEORY

To describe the atom-solid interaction, we use an Anderson-like Hamiltonian given by

$$H(t) = \sum_{\mathbf{kn}, \sigma} \varepsilon_{\mathbf{kn}} \hat{n}_{\mathbf{kn}, \sigma} + \sum_{\sigma} E_a^{\sigma}(t) \hat{n}_{a\sigma} + \sum_{\mathbf{kn}, \sigma} [T_{\mathbf{kn}, a}^{\sigma}(t) \hat{c}_{\mathbf{kn}, \sigma}^{\dagger} \hat{c}_{a\sigma} + T_{a, \mathbf{kn}}^{\sigma}(t) \hat{c}_{a\sigma}^{\dagger} \hat{c}_{\mathbf{kn}, \sigma}], \quad (1)$$

where we are including the presence of several (n) bands to describe the electronic structure of the solid. Thus $\varepsilon_{\mathbf{kn}}$ is the \mathbf{k} eigenstate corresponding to band n and $T_{\mathbf{kn}, a}^{\sigma}(t)$ is the electronic hopping between the localized atom state φ_a and the solid \mathbf{k} state belonging to the band n . Both the atom energy $E_a^{\sigma}(t)$ and the hopping parameters $T_{\mathbf{kn}, a}^{\sigma}(t)$ are obtained from a model for the solid-atom interaction based on a superposition of pair-atom interactions.^{8,9}

To arrive at Eq. (1), we start from a second-quantized many-body Hamiltonian describing a system of interacting atoms, in which terms involving four different spin-orbital indexes are neglected:

$$H = \sum_{i, \sigma} \left\{ \varepsilon_i + \sum_j [J_{ij} \hat{n}_{j-\sigma} + (J_{ij} - J_{ij}^x) \hat{n}_{j\sigma}] \right\} \hat{n}_{i\sigma} + \sum_{i \neq j, \sigma} \left\{ t_{ij} + \sum_m [h_{m,ij} \hat{n}_{m-\sigma} + (h_{m,ij} - h_{m,ij}^x) \hat{n}_{m\sigma}] \right\} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma}. \quad (2)$$

The Hamiltonian parameters in Eq. (2) correspond to the one- and two-electron integrals written in terms of a symmetrically orthonormalized atomic basis set $\{\phi_i\}$ (Ref. 10) (atomic units are used) and are given by

$$\begin{aligned} \varepsilon_i &= \left\langle \phi_i(\mathbf{r}) \left| -\frac{1}{2} \nabla_r^2 - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \right| \phi_i(\mathbf{r}) \right\rangle, & t_{ij} &= \left\langle \phi_i(\mathbf{r}) \left| -\frac{1}{2} \nabla_r^2 - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \right| \phi_j(\mathbf{r}) \right\rangle, \\ J_{ij} &= \left\langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_j(\mathbf{r}') \phi_i(\mathbf{r}) \right\rangle, & J_{ij}^x &= \left\langle \phi_i(\mathbf{r}) \phi_j(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_i(\mathbf{r}') \phi_j(\mathbf{r}) \right\rangle, \\ h_{m,ij} &= \left\langle \phi_m(\mathbf{r}) \phi_i(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_j(\mathbf{r}') \phi_m(\mathbf{r}) \right\rangle, & h_{m,ij}^x &= \left\langle \phi_m(\mathbf{r}) \phi_i(\mathbf{r}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \phi_m(\mathbf{r}') \phi_j(\mathbf{r}) \right\rangle. \end{aligned} \quad (3)$$

Making a mean-field approximation in Eq. (2), assuming the atom-solid system as a diatomic one in which one atom has a continuous basis set $\{\varphi_{\mathbf{kn}}\}$, and neglecting cross terms involving states on the same ‘‘atom,’’ we can write the interaction Hamiltonian in Anderson form:

$$\begin{aligned} H(t) &= \sum_{\mathbf{kn}, \sigma} \varepsilon_{\mathbf{kn}} \hat{n}_{\mathbf{kn}, \sigma} + \sum_{\sigma} \left\{ \varepsilon_a + J_{aa} \langle n_{a-\sigma} \rangle + \sum_{\mathbf{kn}} [J_{a, \mathbf{kn}} \langle n_{\mathbf{kn}, -\sigma} \rangle + (J_{a, \mathbf{kn}} - J_{a, \mathbf{kn}}^x) \langle n_{\mathbf{kn}, \sigma} \rangle] \right\} \hat{n}_{a\sigma} \\ &+ \sum_{\mathbf{kn}, \sigma} \left\{ \left[t_{a\mathbf{kn}} + (J_{a\mathbf{kn}} - J_{a\mathbf{kn}}^x) \langle c_{a\sigma}^{\dagger} c_{\mathbf{kn}, \sigma} \rangle + h_{a, a\mathbf{kn}} \langle n_{a-\sigma} \rangle + (h_{a, a\mathbf{kn}} - h_{a, a\mathbf{kn}}^x) \langle n_{a\sigma} \rangle \right. \right. \\ &\left. \left. + \sum_{\mathbf{k}'n', \sigma} [h_{\mathbf{k}'n', a\mathbf{kn}} \langle n_{\mathbf{k}'n', -\sigma} \rangle + (h_{\mathbf{k}'n', a\mathbf{kn}} - h_{\mathbf{k}'n', a\mathbf{kn}}^x) \langle n_{\mathbf{k}'n', \sigma} \rangle] \right] \hat{c}_{\mathbf{kn}, \sigma}^{\dagger} \hat{c}_{a\sigma} + \text{H.c.} \right\}. \end{aligned} \quad (4)$$

The time dependence of this Hamiltonian arises from the motion of the projectile along its trajectory, which leads to time-dependent interaction parameters. In Eq. (4) we have neglected the energy shifts of the eigenstates of the unperturbed solid. The next step is to calculate the solid-atom interaction parameters in terms of one- and two-electron atomic integrals. Assuming the \mathbf{kn} states of the solid given as a linear combination of the symmetrically orthonormalized site basis set,

$$\varphi_{\mathbf{kn}} = \sum_{\mu, j} \mathbf{C}_{\mu j}^{\mathbf{kn}} \varphi_{\mu}(\mathbf{r} - \mathbf{R}_j),$$

with μ and j denoting orbital and site, respectively. Neglecting the off-diagonal terms of the local partial density of states and three-center integrals, the final expressions for $E_a^{\sigma}(t)$ and $T_{\mathbf{kn}, a}^{\sigma}(t)$ are

$$E_a^{\sigma}(t) = \varepsilon_a + J_{aa} \langle n_{a-\sigma} \rangle + \sum_{\mu, j} \{ J_{a, \mu}(\mathbf{R}_j) \langle n_{\mu-\sigma}(j) \rangle + [J_{a\mu}(\mathbf{R}_j) - J_{a\mu}^x(\mathbf{R}_j)] \langle n_{\mu\sigma}(j) \rangle \}, \quad (5)$$

$$T_{\mathbf{kn},a}^\sigma(t) = \sum_{\mu,j} \mathbf{C}_{\mu j}^{\mathbf{kn}} \left(t_{a\mu}(\mathbf{R}_j) + [J_{a\mu}(\mathbf{R}_j) - J_{a\mu}^x(\mathbf{R}_j)] \langle c_{a\sigma}^\dagger c_{\mu\sigma} \rangle + h_{a,a\mu}(\mathbf{R}_j) \langle n_{a-\sigma} \rangle + [h_{a,a\mu}(\mathbf{R}_j) - h_{a,a\mu}^x(\mathbf{R}_j)] \langle n_{a\sigma} \rangle \right. \\ \left. + \sum_{\beta} \{ h_{\beta,a\mu}(\mathbf{R}_j) \langle n_{\beta-\sigma}(j) \rangle + [h_{\beta,a\mu}(\mathbf{R}_j) - h_{\beta,a\mu}^x(\mathbf{R}_j)] \langle n_{\beta\sigma}(j) \rangle \} \right) = \sum_{\mu,j} \mathbf{C}_{\mu j}^{\mathbf{kn}} T_{\mu a}^\sigma(\mathbf{R}_j). \quad (6)$$

Therefore $E_a^\sigma(t)$ and $T_{\mathbf{kn},a}^\sigma$ can be calculated as the superposition of pair interactions between the adsorbate and atoms of the solid ($t_{a\mu}, J_{a\mu}, h_{a,a\mu}, \dots$), weighted by the average occupation numbers $\langle n_{\mu\sigma}(j) \rangle$ of the respective site (j) and orbital (μ). The calculation of the Hamiltonian parameters implies an expansion in the overlaps between the atomic orbitals centered on the several atoms composing the system.⁸

To solve the time-dependent Schrödinger equation for the one-particle Hamiltonian Eq. (4), we use the following Green functions:

$$G_{q\alpha}^\sigma(t, t_0) = -i\Theta(t - t_0) \langle \psi(t_0) | \hat{c}_{\alpha\sigma}^\dagger(t_0) \hat{c}_{q\sigma}(t) + \hat{c}_{q\sigma}(t) \hat{c}_{\alpha\sigma}^\dagger(t_0) | \psi(t_0) \rangle,$$

where $\hat{c}_{\alpha\sigma}^\dagger$ ($\hat{c}_{\alpha\sigma}$) creates (destroys) an electron in an eigenstate φ_α of the Hamiltonian at the initial time t_0 , while $\hat{c}_{q\sigma}^\dagger$ ($\hat{c}_{q\sigma}$) operates over the eigenstates of the atom-solid system without interaction. In the special case of a scattering process, both sets of eigenstates are coincident and include the atom φ_a and the solid $\varphi_{\mathbf{kn}}$ states.

The average occupation number of the projectile state is calculated as⁷

$$\langle n_{a\sigma}(t) \rangle = \sum_{\alpha \text{ occ}} |G_{a\alpha}^\sigma(t, t_0)|^2, \quad (7)$$

where the sum runs over the initially occupied states. The equation of motion for the Green function $G_{q\alpha}^\sigma(t, t_0)$ leads to two kinds of differential equations depending on whether q corresponds to either the atomic a state or the solid \mathbf{kn} state:

$$\frac{d}{dt} G_{a\alpha}^\sigma(t, t_0) = -i \left\{ E_a^\sigma(t) G_{a\alpha}^\sigma(t, t_0) + \sum_{\mathbf{kn}} T_{\mathbf{kn},a}^\sigma(t) G_{\mathbf{kn},\alpha}^\sigma(t, t_0) + \delta(t - t_0) \delta_{a\alpha} \right\}, \quad (8a)$$

$$\frac{d}{dt} G_{\mathbf{kn},\alpha}^\sigma(t, t_0) = -i \{ \varepsilon_{\mathbf{kn}} G_{\mathbf{kn},\alpha}^\sigma(t, t_0) + T_{\mathbf{kn},a}^\sigma(t) G_{a\alpha}^\sigma(t, t_0) + \delta(t - t_0) \delta_{\mathbf{kn},\alpha} \}. \quad (8b)$$

Introducing the phase transformation

$$G_{q\alpha}^\sigma(t, t_0) = g_{q\alpha}^\sigma(t, t_0) \exp \left(-i \int_{t_0}^t E_q^\sigma(\tau) d\tau \right),$$

performing the integration in Eq. (8b), and replacing the result into Eq. (8a), one obtains

$$\frac{d}{dt} g_{a\alpha}^\sigma(t, t_0) = -i \left\{ \int_{t_0}^t d\tau \Sigma^\sigma(t, \tau) g_{a\alpha}^\sigma(\tau, t_0) + \sum_{\mathbf{kn}} \tilde{T}_{a\mathbf{kn}}^\sigma(t) g_{\mathbf{kn},\alpha}^\sigma(t_0, t_0) + \delta(t - t_0) \delta_{a\alpha} \right\}, \quad (8c)$$

where

$$\tilde{T}_{a\mathbf{kn}}^\sigma(t) = T_{a\mathbf{kn}}^\sigma(t) \exp \left(-i \int_{t_0}^t [\varepsilon_{\mathbf{kn}} - E_a^\sigma(\tau)] d\tau \right) \quad (9)$$

and

$$\Sigma^\sigma(t, \tau) = -i\Theta(t - \tau) \sum_{\mathbf{kn}} \tilde{T}_{a\mathbf{kn}}^\sigma(t) \tilde{T}_{a\mathbf{kn}}^\sigma(\tau). \quad (10)$$

Expressions (5) and (6) for $E_a^\sigma(t)$ and $T_{\mathbf{kn},a}^\sigma(t)$ involve the average occupation numbers of the substrate atoms, which are assumed to be those for the unperturbed solid, and the average occupation number of the incoming atom [Eq. (7)], which must be determined consistently with the solutions of Eq. (8c).

In the case of He (He^+), we will assume that there is only one active electron involved in the process, which is trans-

ferred from or to a $1s$ -like localized level whose asymptotic energy value is -24.6 eV. Thus we assume that for He scattering a “spinless picture” is adequate, implying that only one of the spin projections for the parameters is considered. Therefore the probability of neutral (P^0) and ionic (P^+) charge states is calculated as

$$P^0(t) = \langle n_{\text{He}}(t) \rangle,$$

$$P^+(t) = 1 - \langle n_{\text{He}}(t) \rangle.$$

For He^0 incidence, the sum over occupied states in Eq. (7) includes the atomic a state, while it does not in the case of He^+ incidence.

III. MODEL SYSTEM

The substrate is simulated by a tight-binding semi-infinite linear chain of atoms. The eigenvalues $\varepsilon_{\mathbf{kn}}$ and the weight of

the atomic state μ centered on the first atom of the linear chain, which corresponds to the coefficient $C_{\mu 1}^{kn}$ appearing in Eq. (6), are given by

$$\varepsilon_{kn} = \varepsilon_0^{(n)} + 2\beta^{(n)} \cos(\pi x),$$

$$C_{\mu 1}^{kn} = \frac{\sqrt{2} \sin(\pi x)}{\sqrt{1 + 2 \cos(\pi x)}},$$

with x varying between 0 and 1.

For solids with sp -band structure, nonhybridized s - and p -band states are considered, and the hopping parameters $\beta^{(n)}$ are determined from the width of the partial density of occupied states obtained from a realistic band-structure calculation.¹¹ Each band is centered on the respective atomic state energy $\varepsilon_0^{(n)}$, and its occupation is given by the corresponding fraction of one electron. In the case of a localized d band, its energy is located with respect to the extended one according with the electronic band-structure calculations, and the core-level energy is taken from the free-atom calculations considering that the energy shift produced by the presence of the incoming atom can be neglected. The energy parameter $E_{\text{He}}(R)$ and the atom-atom hopping parameter $T_{\mu\text{He}}(R_i)$ with μ running over the s -, p -, and d -like states of the solid, Eqs. (5) and (6), are approximated by those obtained from a self-consistent calculation of the He-metal atom dimer at each internuclear distance R . The time dependence of these Hamiltonian parameters comes from the time variation of R . The energy parameter $E_{\text{He}}(t)$ approximated by the one obtained from the dimer calculation does not differ appreciably from the one calculated from Eq. (5) by considering $\langle n_{\text{He}-\sigma} \rangle = 1$ and the $\langle n_{\mu\sigma} \rangle$ given by the values of the unperturbed solid [Figs. 1(a) and 2(a)].

A. Ga substrate

We assume this system to consist of two nonhybridized bands, one of s nature and the other of p nature. The s band is completely filled, while p band is half-filled. Each band is centered at the respective atomic orbital energy. The d band is considered to be of zero width and located at -0.8 a.u. [see inset of Fig. 1(a)].

B. Ca substrate

Here we consider one band of s nature centered on the atomic s -orbital energy of Ca. The empty states are also assumed of s nature. The $3p_z$ state of Ca located at -1.34 a.u. is the core state which shows an appreciable hybridization with the $1s$ He state in the Ca-He dimer calculation. Therefore it is expected that the $3p_z$ core state of Ca in the He scattering from a Ca surface will play a similar role that the localized d state in the case of Ga [see inset of Fig. 2(a)].

1. Calculation of distances of closest approach

The distances of closest approach, R_c , are obtained from a Molliere-potential approximation to the interaction energy $V(R)$:

$$V(R) = (c/x)[a_1 \exp(-b_1 x) + a_2 \exp(-b_2 x) + a_3 \exp(-b_3 x)],$$

TABLE I. Distance of closest approach, R_c , for several kinetic energies, for the Ga and Ca substrates.

T_c (a.u.)	E_k (keV)	R_c (a.u.) Ga	R_c (a.u.) Ca
8	1.561	0.338	0.234
8.5	1.382	0.371	0.258
9	1.233	0.405	0.283
9.5	1.107	0.440	0.308
10	0.999	0.475	0.333
10.5	0.906	0.510	0.359
11	0.826	0.545	0.385
11.5	0.755	0.580	0.411
12	0.694	0.615	0.438
12.5	0.639	0.649	0.464
15	0.444	0.815	0.596
18	0.308	0.993	0.744
20	0.250	1.097	0.835

with

$$x = R/A, \quad A = \frac{0.885}{(z_1^{2/3} + z_2^{2/3})^{1/2}}, \quad c = \frac{z_1 z_2}{A},$$

and

$$a_1 = 0.35, \quad a_2 = 0.55, \quad a_3 = 0.10,$$

$$b_1 = 0.30, \quad b_2 = 1.80, \quad b_3 = 6.20,$$

where z_1 and z_2 are the projectile and target nuclear charges, respectively, while R is the interatomic distance which within a straight-line trajectory approximation has the following time dependence:

$$R = R_c + |t/T_c|,$$

with T_c the inverse of the projectile velocity. At low incident kinetic energies E_k , we approximate R_c as

$$R_c \approx 1/(b_1/A + B),$$

with

$$B = \frac{E_k - E(\infty)}{a_1 z_1 z_2}.$$

$E(\infty)$ is the total energy of the separated systems. In Table I, R_c is shown for several kinetic energies and for the Ga and Ca substrates.

IV. RESULTS AND DISCUSSION

Figures 1(a) and 2(a) show for Ga and Ca substrates, respectively, the variation with the atom-surface distance R of the Hamiltonian parameter $E_{\text{He}}(R)$ obtained from the self-consistent HF dimer calculation [see Eq. (5)]. It is to be stressed that this $E_{\text{He}}(R)$ parameter is the diagonal $\langle \varphi_a | H | \varphi_a \rangle$ matrix element involving the HF approximation of the interaction potential between the two atoms of the dimer. The pronounced shift downwards observed for small R values is due to the electron-nucleus interaction. Changes from this R dependence are expected in the case where a He

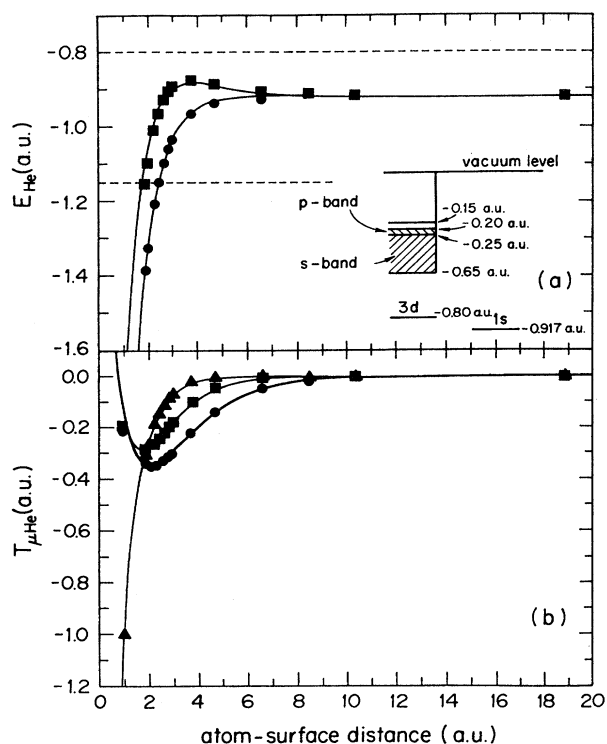


FIG. 1. Ga substrate. (a) Diagonal matrix element $E_{\text{He}}(R)$ as a function of the atom-surface distance: (●) dimer calculation, (■) correction by considering the atomic occupation numbers of the unperturbed solid in Eq. (5). The dashed line indicates the energy location of the solid d -like states (-0.8 and -1.15 a.u.). A schematic diagram of the energy levels involved in the process is also shown. (b) Atom-atom hopping parameter $T_{\mu\text{He}}(R)$ as a function of distance from the surface: (■) $\mu=4s$ -like state (V_s), (●) $\mu=4p$ -like state (V_p), (▲) $\mu=3d$ -like state (V_d).

atom is in front of a metallic surface, this being related to a more efficient electronic screening of the nuclear charges. A better calculation of E_{He} is still desired, although the use of a dimer model to evaluate the Hamiltonian parameters seems to be quite consistent with a linear-chain target. Also shown in Figs. 1(a) and 2(a) is the $E_{\text{He}}(R)$ calculated using expression (5) and considering that the occupation numbers of the atoms of the substrate are fixed by their values in the unperturbed solid. The two forms of calculation lead to negligible differences in the charge-transfer probabilities for all the cases analyzed here. In Fig. 1(b) we show the hopping matrix elements $T_{\text{He}\mu}(R)$ obtained from the dimer He-metal atom calculation as in Eq. (6), between the He $1s$ state and the $4s$, $4p$, and $4d$ Ga states, and in Fig. 2(b) we plot those corresponding to the He $1s$ state and the $4s$ and $3p$ Ca states.

A. Effects of the interaction with a localized state in the target on the charge-exchange process

1. Ga substrate

From Fig. 3 we can observe that (a) the ion survival probability of scattered He^+ is practically 1 along the whole velocity range; (b) the ionization probability of incoming He^0 is

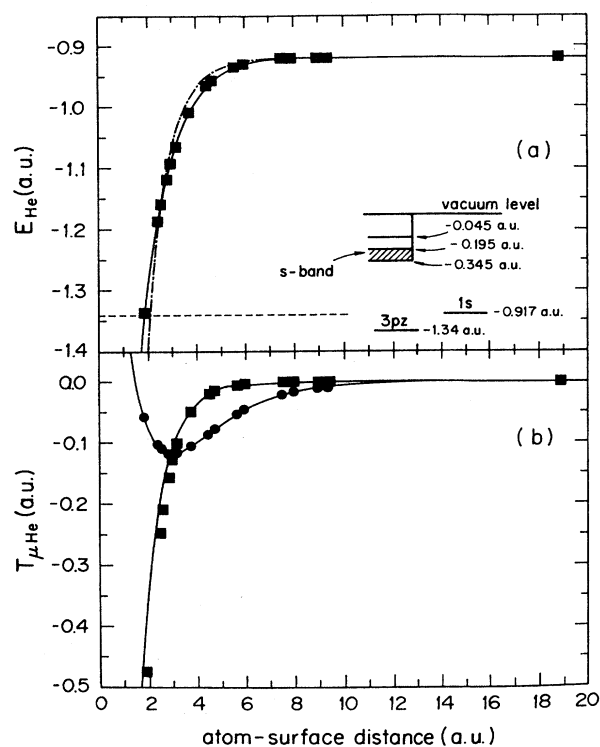


FIG. 2. Ca substrate. (a) The same as in Fig. 1(a): (■) dimer calculation, (dot-dashed line) corrected values, (dashed line) energy location of the $3p$ -core-like state (-1.34 a.u.). (b) The same as in Fig. 1(b): (●) $\mu=4s$ -like state (V_s), (■) $\mu=3p$ core-like state (V_p).

negligible, in agreement with the experimental trends.^{2,3} There are no appreciable differences by omitting the interaction with the localized d band ($V_d=0$ in the figures). Then, in this case, the hybridization between the localized d state and the He $1s$ state does not favor the charge-exchange process. Why is that one expects this hybridization to play an important role in promoting the charge transfer? This is because at low velocities the dynamical collisional process can be visualized as a quasiadiabatic interaction between the atom and localized state in the solid, leading to the formation of bonding and antibonding levels. The antibonding state has chances of being energetically resonant with the band, thus favoring the charge transfer.¹² However and in addition, this possibility is strongly dependent on the weight of the He $1s$ state in the antibonding level. In the Ga case the weight of the d state is predominant along the whole trajectory, because it has a lower binding energy than the He $1s$ level. Thus we can understand the low values for the He^+ neutralization and He ionization probabilities shown in Fig. 3. The same calculation was repeated considering the d state located below the energy of the He $1s$ state. The value $E_d=-1.15$ a.u. was chosen to emulate roughly a Ge target. In this case we obtain an important increase in the neutralization probability for incoming He^+ at low velocities, and also the ionization of He becomes appreciable in this velocity range. These results are clearly due to the hybridization between the d and He $1s$ localized states, giving rise to an antibonding

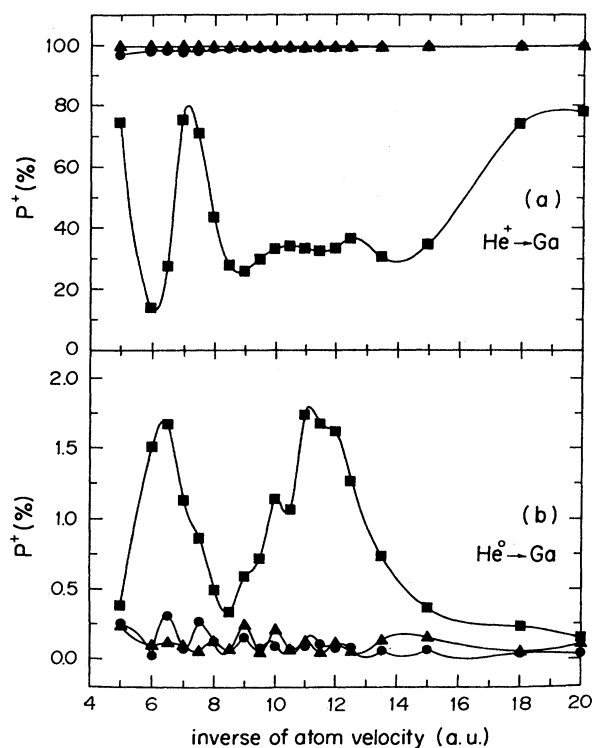


FIG. 3. Ga substrate. (a) Ionization probability as a function of the inverse of projectile velocity for He^+ incidence: (●) $E_d = -0.8$ a.u., (■) $E_d = -1.15$ a.u., (▲) d -like state is not considered ($V_d = 0$). (b) The same as in (a) for He^0 incidence.

level with a predominant weight of the helium state. The behavior of P^+ as a function of the velocity depends on the variation of the antibonding energy along the particle trajectory and also on the bandwidth of the occupied and empty states in the solid.⁷

2. Ca substrate

Here the hybridization of the helium state with the Ca $3p_z$ core level is clearly responsible for the important charge transfer observed at low velocities (Fig. 4). The energy location of the $3p_z$ level (-1.34 a.u.) leads to a very significant He $1s$ weight in the antibonding state, justifying the results obtained. The large (re-)ionization found as the threshold energy ($E_{\frac{1}{2},3} = 250$ eV) is consistent with the experimental findings.^{2,3}

B. "Two-stage" model calculation

We maintain that this kind of time-dependent collisional processes at low kinetic energies of the projectile can be thought of as occurring in two stages: (i) The first one concerns the interaction between helium and the localized state in the solid, resulting in the formation of bonding and antibonding states, and (ii) the second stage is related to the charge exchange taking place between them and the extended band states. The occupation of the He $1s$ state is determined asymptotically by the occupation of either the

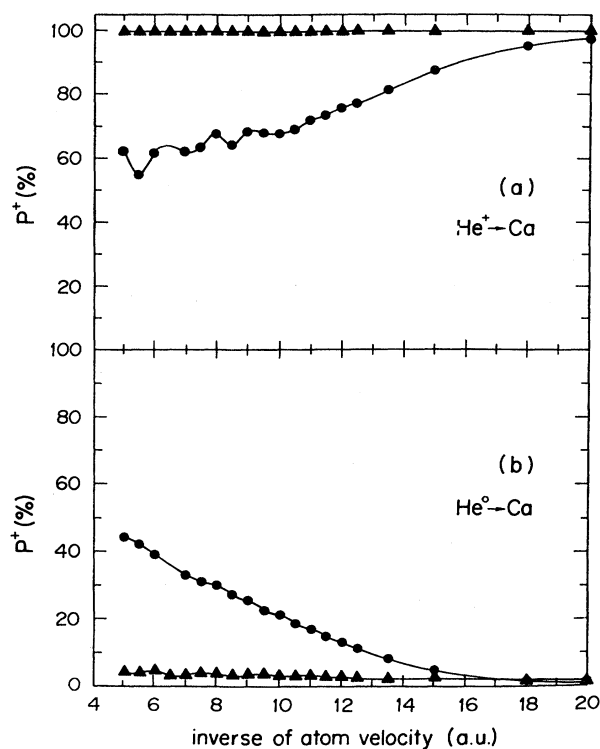


FIG. 4. Ca substrate. (a) Ionization probability as a function of the inverse of projectile velocity for He^+ incidence: (●) $E_{3p} = -1.34$ a.u., (▲) $3p$ -core-like state is not considered ($V_p = 0$). (b) The same as in (a) for He^0 incidence.

bonding or the antibonding orbital, depending on the location of the energy of the He $1s$ state with reference to the localized level in the solid. We have carried out a model calculation to prove that this nonstandard picture within a dynamical process accounts correctly for the mechanisms responsible for the charge exchange in the scattering of He at low kinetic energies. The detailed equations are developed in the Appendix. In Fig. 5 the results for the ionization probability of incoming neutral atoms obtained with this model are compared with those obtained from an exact treatment in which all the interactions are considered on the same footing. The good agreement between both calculations at low incident kinetic energies supports the role played by the localized state in the solid, as an "intermediary agent" in the charge exchange between the projectile and the surface.

C. Contributions of extended and localized states of the solid to ion neutralization

The results depicted in Fig. 6 show the characteristic oscillatory behavior at large velocities due to the nonadiabatic charge exchange between the He $1s$ level and the localized state.^{1,5} At low velocities this charge exchange becomes negligible, but there is an important contribution of the band states to the neutralization, precisely due to the hybridization with a localized state in the solid which has a larger binding energy than the helium state.

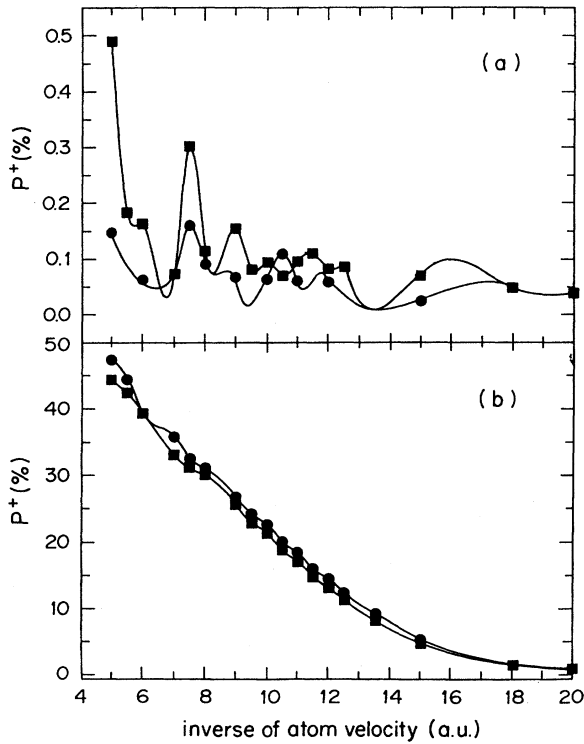


FIG. 5. Ionization probability of incident He^0 as a function of the inverse of projectile velocity: (a) Ga substrate, (■) exact calculation, (●) approximated calculation described in the Appendix. (b) The same as in (a) for a Ca substrate.

D. Velocity dependence of the ionization probability when neglecting the variation of the He 1s level energy

In Fig. 7 we compare the results of He ionization probability considering the helium energy level given by the self-consistent HF dimer calculation [Figs. 1(a) and 2(a)] with those obtained by considering a constant $E_{\text{He}} = -0.917$ a.u. along the whole trajectory. In the case of a Ga target, both calculations lead to a negligible ionization probability at low velocities. The Ca case [Fig. 7(b)] shows that to neglect the changes of the helium energy level by the interaction with the solid atoms results in a poor approximation, leading to unexpected large ionization probabilities at very low incident kinetic energies. This is due to the marked He nature of the antibonding state at small distances from the surface.

E. Target dependence of the relation between ionization probabilities for ion and neutral incoming particles

We have calculated the relation between P^+ for He^0 incidence and P^+ for He^+ incidence (I^0/I^+) for Ga-He and Ca-He systems at a kinetic energy $E_k = 1$ keV. This relation calculated for the case of Ga with E_d located at -1.15 a.u. emulates a Ge target. Our results compare well with measured values³ (Fig. 8).

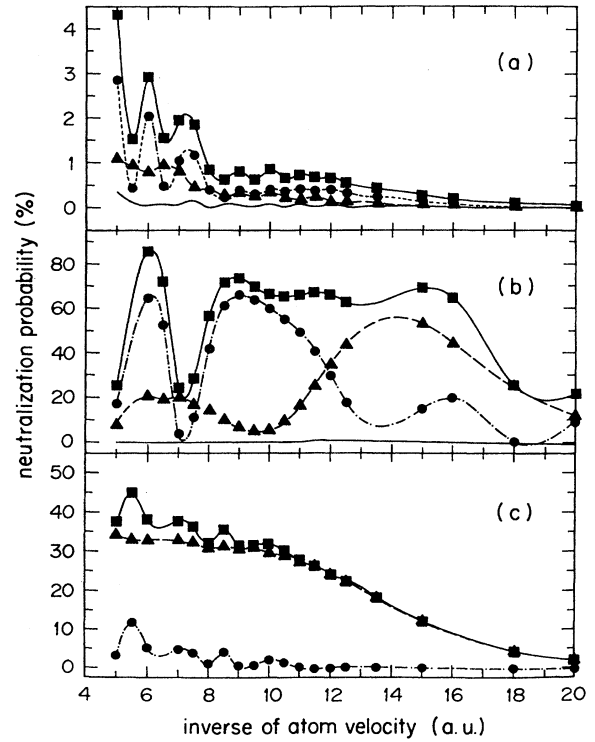


FIG. 6. Contribution of the extended and localized states in the solid to the neutralization of incident He^+ as a function of the inverse of projectile velocity: (a) Ga substrate, $E_d = -0.8$ a.u., (■) total neutralization probability, (▲) *s*-band contribution, (solid line) *p*-band contribution, (●) *d*-band contribution. (b) The same as in (a) for a Ga substrate with $E_d = -1.15$ a.u. (c) Ca substrate, (■) total neutralization probability, (▲) *s*-band contribution, (●) *3p*-core-like state contribution.

V. SUMMARY

To summarize, we conclude that the localized states in solids which hybridize appreciably with the He 1s orbital and have larger binding energies than this state promote the charge transfer in the low-energy scattering of He from solid surfaces. Our results have been obtained by using a time-dependent Anderson Hamiltonian which includes localized and extended states in the solid, and the interaction parameters are extracted from a HF self-consistent calculation of the He-target-atom dimer, thus accounting for a realistic description of the system.

According with this picture we expect, for instance, an important re-ionization in the case of a Ti target having a threshold energy similar to that for a Ca target, because of the presence of the *3p*-corelike state. On the other hand, for Cd the energy of the *4p*-core state is located so deep with respect to the He state that re-ionization will require very high kinetic energies to occur. In cases such as Mg and Na, the *2p*-core orbital will be the responsible of an appreciable re-ionization. For an In substrate, the localized *4d* level is practically resonant with the He 1s state. Therefore, taking into account the downward shift of the helium energy [Figs.

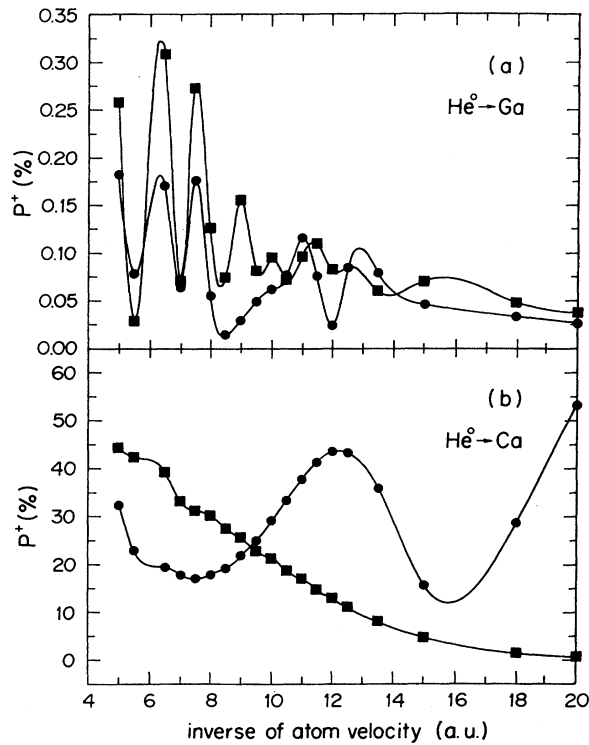


FIG. 7. Ionization probability of incident He^0 as a function of the inverse of projectile velocity: (a) Ga substrate, (■) with $E_{\text{He}}(R)$ varying according with Eq. (5), (●) with $E_{\text{He}}(R) = -0.917$ a.u. (b) The same as in (a) for a Ca substrate.

1(a) and 2(a)], the antibonding state will have a predominant $4d$ nature at distances close to the surface. This is expected to lead to a negligible re-ionization, while for the Sn case the binding energy of the localized $4d$ state is larger than the one for He $1s$ level, although the energy difference between both states is not large enough to define an antibonding state with a clear dominant He nature along the atom trajectory. Thus we expect here a not very important re-ionization as happens in the Ge case.

We have arrived at similar conclusions than those advanced by Tsuneyuki and Tsukada⁶ based on an strictly stationary description of the dimeric systems, but our formalism allows us to solve the dynamical aspects of the collisional process, providing a quantitative method to answer questions about why re-ionization is observed in cases such as Ca and Sn, while this is not to be expected in cases such as Ga and In as shown by the experimental results.

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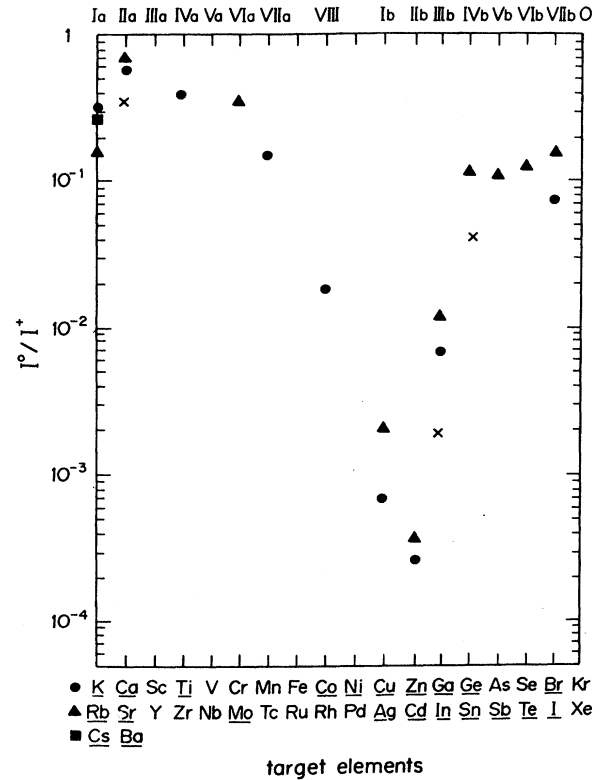


FIG. 8. He^+ intensity by He^0 incidence relative to that by He^+ incidence (I^0/I^+) at a kinetic energy of 1 keV, for several target elements: (●), (▲), (■) measured values (Ref. 2), (×) calculated values.

APPENDIX

The atom-surface scattering process is simulated through the following two stages: (1) The “atomic state” with an energy level given by $E_{\text{He}}(R)$ interacts with the localized solid state of energy E_d through the hopping $T_{d\text{He}}(R)$. This interaction gives rise to bonding and antibonding states. The energy and weight of the atomic He state in the antibonding state are

$$E_A(R) = \frac{E_{\text{He}}(R) + E_d}{2} + \sqrt{\frac{[E_{\text{He}}(R) - E_d]^2}{4} + V_d^2(R)},$$

$$|a_{\text{He}}^A(R)|^2 = \frac{V_d^2(R)}{V_d^2(R) + [E_{\text{He}}(R) - E_A(R)]^2},$$

while for the bonding state these are

$$E_B(R) = \frac{E_{\text{He}}(R) + E_d}{2} - \sqrt{\frac{[E_{\text{He}}(R) - E_d]^2}{4} + V_d^2(R)},$$

$$|a_{\text{He}}^B(R)|^2 = \frac{V_d^2(R)}{V_d^2(R) + [E_{\text{He}}(R) - E_B(R)]^2}.$$

(2) The bonding and antibonding states interact with the extended states of the solid, and the dynamical process of charge transfer can be calculated from an Anderson time-dependent Hamiltonian in the form

$$\begin{aligned}
 H(t) = & \sum_{\mathbf{k}, \sigma} \varepsilon_{\mathbf{k}\sigma} \hat{n}_{\mathbf{k}\sigma} + E_A(R) \hat{n}_A + E_B(R) \hat{n}_B \\
 & + \sum_{\mathbf{k}, \sigma} [T_{\mathbf{k}A}(R) \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{A\sigma} + T_{A\mathbf{k}}(R) \hat{c}_{A\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma}] \\
 & + \sum_{\mathbf{k}, \sigma} [T_{\mathbf{k}B}(R) \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{B\sigma} + T_{B\mathbf{k}}(R) \hat{c}_{B\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma}].
 \end{aligned}$$

Here the hopping parameters $T_{\mathbf{k}A}(R)$ and $T_{\mathbf{k}B}(R)$ are taken as

$$T_{\mathbf{k}A}(R) = a_{\text{He}}^A(R) T_{\mathbf{k}\text{He}}(R),$$

$$T_{\mathbf{k}B}(R) = a_{\text{He}}^B(R) T_{\mathbf{k}\text{He}}(R),$$

because the hopping between \mathbf{k} states and the localized d state is zero; $T_{\mathbf{k}\text{He}}$ is given by Eq. (6).

Finally, the He occupation number $\langle n_{\text{He}}(t) \rangle$, obtained from the occupations of the bonding and antibonding states, are given by

$$\langle n_{\text{He}}(t) \rangle \equiv |a_{\text{He}}^A|^2 \langle n_A(t) \rangle + |a_{\text{He}}^B|^2 \langle n_B(t) \rangle.$$

Asymptotically, if the localized state in the solid has a lower binding energy than the He $1s$ state, we have $\langle n_{\text{He}}(\infty) \rangle = \langle n_B(\infty) \rangle$, while in the opposite case we have $\langle n_{\text{He}}(\infty) \rangle = \langle n_A(\infty) \rangle$.

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