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Close-coupling calculations for ion–surface interactions

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Abstract

The time-dependent close-coupling equations for the ion–jellium-surface system are solved both by means of a *fixed-ion* self-energy formalism and by direct integration. The self-energies yield non-perturbative level shifts and widths, as well as information about the formation of hybrid orbitals in the combined potentials of ion and surface. Convergence of the self-energy results is achieved within a small set of discrete hydrogenic basis functions centered on the ion. In general, the calculated level shifts and widths are in good agreement with the results of other theoretical investigations. The direct time integration is applied in an exploratory study to the dynamics of hollow-atom formation in surface interactions of highly charged ions.

Keywords: Ion–surface interactions; Close-coupling calculations; Ionization; Neutralization; Hollow atom

1. Introduction

The detailed understanding of electronic processes that take place in ion–metal surface interactions has been of considerable interest during the past decade [1]. Using a two-center expansion with hydrogenic states on the ion site and jellium states for the metal half-space, we solve the close-coupling equations for the ion-metal surface system by eliminating the explicit dependence on the conduction-band states. In fixed-ion approximation, this elimination leads to a complex non-Hermitian self-energy matrix whose eigenvalues determine (via their real parts) the energies and (via their imaginary parts) the widths of the ionic resonances evolving from the asymptotic ionic states [2,3]. We use atomic units throughout this paper.

2. Self-energy method

We solve the time-dependent one-electron Schrödinger equation by expanding the total one-electron wave function as

$$|\Psi\rangle = \sum_i^{\mathrm{N}} a_i(t)|\psi_i\rangle + \int\limits_{k \leqslant k_{\max}} \rho(\boldsymbol{k}) b_{\boldsymbol{k}}(t)|\phi_{\boldsymbol{k}}\rangle\,\mathrm{d}\boldsymbol{k}, \qquad (1)$$

where $\{|\psi_i\rangle\}$ are the hydrogenic wave functions at the ion-site, $\{|\phi_{\boldsymbol{k}}\rangle\}$ are the step-potential eigenstates in the metal half-space, and $\rho(\boldsymbol{k})$ is the corresponding density of states. Inserting the ansatz (1) into the Schrödinger equation yields two sets of coupled differential equations:

$$\begin{aligned} i\dot{a}_j(t) = {} & \sum_i a_i(t)\langle\psi_j|H|\psi_i\rangle \\ & + \int\limits_{k\leqslant k_{\max}} \rho(\boldsymbol{k}) b_{\boldsymbol{k}}(t)\langle\psi_j|H|\phi_{\boldsymbol{k}}\rangle\,\mathrm{d}\boldsymbol{k} \\ & - i\int\limits_{k\leqslant k_{\max}} \rho(\boldsymbol{k}) \dot{b}_{\boldsymbol{k}}(t)\langle\psi_j|\phi_{\boldsymbol{k}}\rangle\,\mathrm{d}\boldsymbol{k}; \\ & j = 1,\ldots,N; \end{aligned} \qquad (2)$$

$$\begin{aligned} i\dot{b}_{\boldsymbol{k}'}(t) = {} & \sum_i a_i(t)\langle\phi_{\boldsymbol{k}'}|H|\psi_i\rangle \\ & + \int\limits_{k\leqslant k_{\max}} \rho(\boldsymbol{k}) b_{\boldsymbol{k}}(t)\langle\phi_{\boldsymbol{k}'}|H|\phi_{\boldsymbol{k}}\rangle\,\mathrm{d}\boldsymbol{k} \\ & - i\sum_i \dot{a}_i(t)\langle\phi_{\boldsymbol{k}'}|\psi_i\rangle; \quad k \leqslant k_{\max}. \end{aligned} \qquad (3)$$

The initial conditions are

$$a_j(-\infty) = a_j^{(0)}, \qquad (4)$$

$$b_{\boldsymbol{k}}(-\infty) = b_{\boldsymbol{k}}^{(0)}. \qquad (5)$$

In a first approach we perform a Laplace transformation [2,3] of the coupled equations (2) and (3), neglect the motion of the ion, and eliminate the explicit dependence on the coefficients $b_{\boldsymbol{k}}(t)$ by formally integrating Eq. (3) and inserting the resulting expression for $b_{\boldsymbol{k}}(t)$ into Eq. (2). This leads to the complex non-Hermitian self-energy in *fixed-ion*

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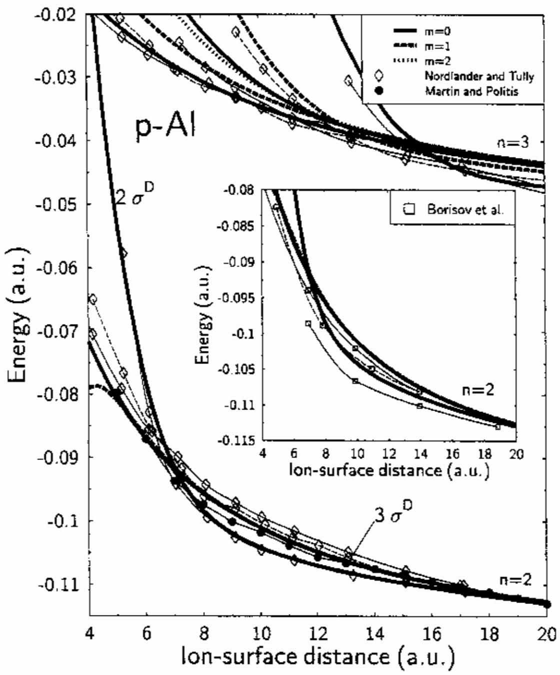

Fig. 1. Adiabatic energies for the $n = 2, 3$ manifold of the p-Al system compared with results of Nordlander and Tully [8], Martín and Politis [10] and Borisov et al. [6,7]. Thick lines: present result; solid line: $m = 0$, dashed line: $m = 1$, short-dashed line: $m = 2$.

approximation whose matrix elements in the ionic subspace are given as

$$\begin{aligned} S_{ij}(s) = {} & \varepsilon_i \delta_{ij} + \langle \psi_i \mid V_f \mid \psi_j \rangle \\ & + \mathcal{P} \int\limits_{k \leqslant k_{\max}} \mathrm{d}\boldsymbol{k}\, \rho(\boldsymbol{k}) \frac{\left(N_i^*(\boldsymbol{k})(\varepsilon_k - is) + W_i^*(\boldsymbol{k}) \right)}{(is - \varepsilon_k)} \\ & \times \left(N_j(\boldsymbol{k})(\varepsilon_k - is) + W_j(\boldsymbol{k}) \right) \\ & - i\pi \int\limits_{k \leqslant k_{\max}} \rho(\boldsymbol{k}) W_i^*(\boldsymbol{k}) W_j(\boldsymbol{k}) \delta(is - \varepsilon_k)\, \mathrm{d}\boldsymbol{k}, \quad (6) \end{aligned}$$

with

$$N_i(\boldsymbol{k}) := \langle \phi_k \mid \psi_i \rangle,$$

$$W_i(\boldsymbol{k}) := \langle \phi_k \mid V_i \mid \psi_i \rangle,$$

and the principal part denoted by $\mathcal{P}$. Additionally, we apply the Wigner–Weisskopf pole approximation [2,3] in Eq. (6) by choosing

$$s := s_{ij} = -\tfrac{1}{2} i \left(\varepsilon_i + \varepsilon_j \right).$$

A convenient decomposition of the various terms of the self-energy (6) was achieved by rewriting the total one-particle Hamilton operator as a sum of channel Hamiltonians and their corresponding perturbations [2–5]

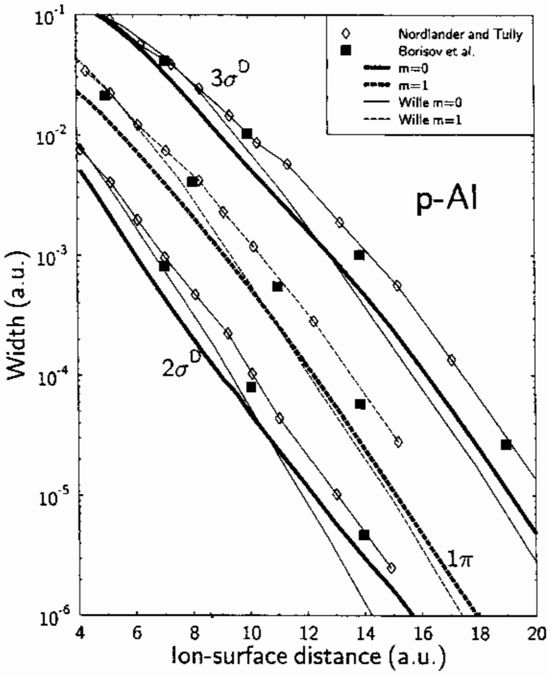

Fig. 2. Adiabatic widths for the $n = 2$ manifold of the p-Al system compared with theoretical results of Wille [9], Nordlander and Tully [8], and Borisov et al. [6,7]. Line type for $m = 0, 1$ as in Fig. 1.

$$H = H_i + V_i = H_f + V_f. \quad (7)$$

The channel Hamilton operators and corresponding channel perturbations are given by

$$H_i = -\tfrac{1}{2}\nabla^2 + V_{\text{step}},$$

$$V_i = V_C^> + V_{\text{image}}^N + V_{\text{image}}^e,$$

$$H_f = -\tfrac{1}{2}\nabla^2 + V_C,$$

$$V_f = V_{\text{step}} + V_{\text{image}}^N + V_{\text{image}}^e - V_C^<,$$

where $V_C^>$ and $V_C^<$ are the Coulomb potential in the vacuum and metal half-space, respectively. V_{image}^N and V_{image}^e are the nuclear image and self-image potential acting on the electron, respectively. Details of the evaluation of matrix elements of the self-energy and an extensive study for the p-Al system are presented in Refs. [3,5].

The basis functions $\{|\psi_i\rangle\}$ are eigenfunctions of H_f whereas the basis functions $\{|\phi_k\rangle\}$ are eigenfunctions of the initial channel Hamilton operator H_i, where V_{step} represents a potential step at the electronic surface. The height of this step (0.585 a.u. for Al) equals the energetic location of the conduction band bottom with respect to the ionization threshold [5].

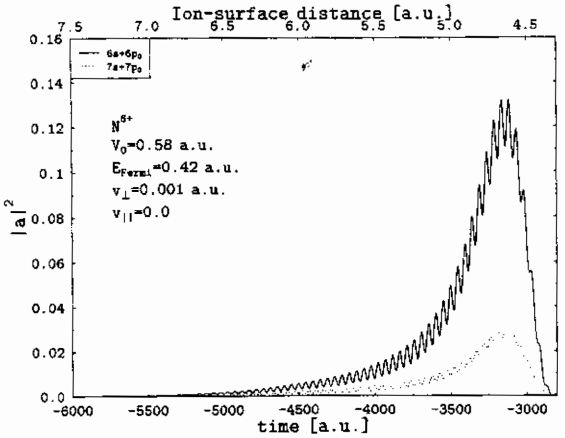

Fig. 3. Population dynamics for the $n = 6, 7$ states of N^{6+} with a step potential of depth $V_0 = 0.585$ a.u.

The adiabatic complex self-energies $\mathcal{S}_i = \mathrm{Re}(\mathcal{S}_i) + i\,\mathrm{Im}(\mathcal{S}_i)$ are obtained by diagonalizing (6) in a hydrogenic basis set. The real parts $\mathrm{Re}(\mathcal{S}_i)$, the adiabatic single-particle energies of hybrid states, are shown in Fig. 1 for the p-Al system. The labels $\sigma, \pi, \delta, \ldots$ refer to the m quantum number which is the only good quantum number characterizing the adiabatic states. At each avoided crossing of two states the wavefunctions of the adiabatic states involved change quite significantly. At any finite velocity of the projectile the electron would therefore diabatically follow the energy curves. For the width (Fig. 2), given as $\Gamma = -2\,\mathrm{Im}(\mathcal{S}_i)$, of the asymptotic $n = 2$ manifold we therefore show the *diabatized* adiabatic widths of the $2\sigma^D$, $3\sigma^D$ and additionally the 1π state. Using the 1s–5g$_4$ hydrogenic basis we find good agreement with various other calculations [6–10] for the adiabatic energies whereas the discrepancies for the adiabatic width reflect the different choices of the surface potential and the strong sensitivity of the width (which describes resonant electron tunneling through the surface potential barrier) to details of the potential. The calculations performed by Nordlander and Tully [8] and Borisov et al. [6,7] involved a smeared surface potential having a width of about 1 a.u. In these calculations the loosely bound jellium states have a *delayed* exponential decay starting at $D \approx 1$ a.u. according to our definition of the ion–surface distance, whereas in our calculations all jellium wave functions begin to decay at $D = 0$. This *delayed* exponential decay leads to a stronger interaction with the bound ionic states and explains the larger widths found in Refs. [6–8].

3. Close-coupling calculations

In a second approach we directly integrate the time-dependent one-electron Schrödinger equation after eliminating the explicit conduction-band dependence. Neglecting the overlap between ionic and conduction-band states, Eqs. (2) and (3) become

$$
\begin{aligned}
i\dot{a}_l(t) &= \sum_i a_i(t)\mathcal{F}_{il}(t) \\
&\quad -i\sum_i a_i(t)\int_0^{k_{\max}} \mathrm{d}\boldsymbol{k}\,\rho(\boldsymbol{k})W_l^*(\boldsymbol{k},t)W_i(\boldsymbol{k},t) \\
&\quad + \int_0^{k_{\mathrm{Fermi}}} \mathrm{d}\boldsymbol{k}\,\rho(\boldsymbol{k})W_l^*(\boldsymbol{k},t)b_{\boldsymbol{k}}(0); \\
&\quad l = 1,\ldots,N;
\end{aligned}
\tag{8}
$$

with

$$\mathcal{F}_{il}(t) = \langle \psi_l(\boldsymbol{r}) \mid V_f \mid \psi_i(\boldsymbol{r})\rangle\, \mathrm{e}^{-i(\varepsilon_i-\varepsilon_l)t}, \tag{9}$$

$$W_i(\boldsymbol{k},t) = \langle \psi_{\boldsymbol{k}}(\boldsymbol{r}) \mid V_i \mid \psi_i(\boldsymbol{r})\rangle\, \mathrm{e}^{-i(\varepsilon_i-\varepsilon_k)t}, \tag{10}$$

where we have approximated the non-local propagator by its local counterpart. In a first feasibility test we opt for the model collision system where N^{6+} interacts with a surface having a potential depth of $V_0 = 0.585$ a.u. and a Fermi energy of $E_{\mathrm{Fermi}} = 0.42$ a.u. For large ion–surface distances the $n = 6$ states are the highest manifold in resonance with the occupied part of the conduction band. We solve Eq. (8) in the $\{6s, 6p_0, 7s, 7p_0\}$ subspace. We chose the s- and p-states as a basis in our close-coupling calculation since these states interact much stronger with the surface than states with large l and m quantum number [5]. Fig. 3 shows the population dynamics of these levels for perpendicular incidence with $v_\perp = 0.001$ a.u. on the incoming trajectory. As we do not include multi-electron effects in our approach we focus on the very first capture events at large ion–surface distances that initiate the formation of hollow ions [11]. Subshell populations have been added according to $(|a_{6s}|^2 + |a_{6p_0}|^2)$ and $(|a_{7s}|^2 + |a_{7p_0}|^2)$. One clearly sees the dominant electron flux into the $n = 6$ manifold, a strong increase setting in at $D \approx 6.5$ a.u. which roughly correlates to the classical radius $\langle r\rangle_6$. The $n = 7$ manifold, which is not in resonance with the occupied part of the conduction band is essentially fed through coupling with the $n = 6$ states. Within our model, a depopulation of the $n = 6$ manifold sets in at $D \approx 4.7$ a.u. which is related to the n=6 state being shifted above the Fermi energy. We plan to extend our time-dependent calculations by systematically (i) increasing the basis set, (ii) including overlap corrections, (iii) including the full, non-local propagator in (8), and (iv) including translation factors that are of relevance for grazing collisions with large projectile velocity components parallel to the surface [12].

4. Concluding remarks

In this work we have presented results for single-particle electronic processes in ion–surface collisions achieved both in *fixed-ion approximation* by studying eigenvalues of the complex self-energy matrix and by solving the time-dependent close-coupling equations. From the self-energy calculations we obtained adiabatic single-particle energies and resonance widths of dressed ionic states which are in good overall agreement with results from other non-perturbative methods. The remaining discrepancies are attributed mainly to different choices for the electronic potentials. The solution of the close-coupling equations for N^{6+} interacting with a step potential of depth $V_0 = 0.585$ a.u. revealed that capture of electrons in specific n-manifolds takes place when the ion–surface distance falls below roughly the classical orbital radius $\langle r \rangle_n$.

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