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Perturbative treatment of electronic correlations in time-dependent collision processes

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Abstract. The Green function formalism introduced by Keldysh for irreversible processes is applied to the calculation of the time-dependent charge exchange probabilities in scattering problems. Considering the initial state of two non-interacting subsystems described by an independent particle model, their interaction is taken in a first stage, as evolving in time according to a time-dependent Hartree–Fock (TDHF) scheme. The equations of motion for the two-times Green functions are subsequently obtained in Dyson-like form by including the residual electronic correlations expanded perturbatively up to second order. It is shown that, by solving these equations of motion, this in turn allows one to calculate the two-particle correlation functions at equal times, as required to describe the fractions of charge in each subsystem. This procedure contrasts with that of considering expectation values of the correlation functions taken between the corrected TDHF state up to an equivalent order in the perturbation. In order to test the advantages of this method we have applied this scheme to the scattering of an atom from a three-substrate atom chain described by an Anderson Hamiltonian, where comparisons with exact solutions can be easily established. We found that, in this case, the fractions of charges carried by the scattered particle obtained with our proposal compare fairly well with exact results, within an ample range of parameter selection.

1. Introduction

In recent years the scattering of ions or atoms with simple structures such as H^+ , D^+ , He^+ and He^0 , from a large variety of surface samples in the form of either pure elements or compounds [1–10], has received considerable attention. One of the main reasons for this is the kind of high-quality experimental data that can be collected for scattering of different sorts of projectile from well defined solid surfaces. The theoretical modelling of the charge exchange processes occurring during the projectile–target interaction has been largely based on using the Anderson (or Anderson–Newns, in its independent particle version) Hamiltonian. Several aspects of this model have been investigated in relation to the final charge state of the projectile, ranging from the effects of the finite band width of the solid electronic states against the infinite-band-width limit assumption [11], the influence of the presence of localized or core surface states, the importance of the variations in the parameters entering the Hamiltonian as well as the adjustment of the projectile’s velocity consistently with the electronic transitions taking place along the trajectory [12, 13]. Also studies on the electronic excitations produced by deep-level promotion occurring during the collision process have been recently [14] carried out along these lines. Most of these have been done within an independent particle or time-dependent Hartree–Fock (TDHF) basis under

the Anderson–Newns model. The effects of the electronic on-site electronic correlation have been considered, in some cases, to be those arising from an infinite correlation energy [15, 16], thus precluding the description of the different charge states of the projectile on the same footing. In other cases, the effects of the electronic correlation have been treated within perturbation theory [17–19]. Sebastian [17] made detailed studies on these effects in ion scattering using a time-dependent coupled-cluster approach (CCA). This method, although very attractive, has several difficulties as it does not provide an efficient way for computing the expectation values of the operators related to the charge state of the scattered particle. On the other hand, truncation of expressions (equation 12 in [17]) causes problems in the normalization of the final state and also it is not simple to apply particularly for systems where a large number of active states are present, requiring one to solve a large set of coupled differential equations. Goldberg and Flores [18] (hereafter referred to as I) adopted a different approach based on a perturbative expansion in terms of the residual electronic interaction that remains after performing the TDHF approximation. These calculations were based on the use of the Keldysh [20] Green functions formalism and applied to a time-dependent Anderson description of atoms emitted from a solid surface. In this case, only the electronic repulsion at the adatom site was considered. The atomic charge-state probabilities were extracted from the asymptotic behaviour of the Green functions, a clear and straightforward procedure when a symmetric Anderson condition, i.e. $\varepsilon_a = -U/2$, and a restricted Hartree–Fock (HF) description for the time evolution of the zeroth-order wavefunction are considered. In such cases the second-order correction to the self-energies reproduces the exact differences between energies of the N and $N \pm 1$ many-particle states in the uncoupled atom–substrate limit. Another approach for extended systems based on previous work on the Kondo problem has been put forward by Marston *et al* [21] after experiments on the neutralization of Li, Na and K ions scattered from clean Cu(001) surfaces. In this scheme the whole of the available Hilbert space is truncated so as to consider a selected, and in principle relevant, set of many-body configurations. This method was applied to these experiments with results that exhibit the right trends but show no improvements with respect to calculations based on the standard single-particle model.

In collision processes between atoms or ions and solid surfaces, one is concerned with the calculation of the asymptotic charge-state fractions of the intervening subsystems. This can be accomplished by using selected correlation functions able to pick up specific charge states from all the configurations contained in the final state. These can be straightforwardly obtained in an independent particle scheme [22] but, in the presence of contributions such as the inter- or intra-site direct and exchange terms as generated by the Coulomb interaction, this is no longer an easy task. One purpose of this work is to extend the use of real-time Green function methods in the field of time-dependent phenomena, allowing for a general treatment of the two-particle interaction potential. As in I, a perturbative approach is adopted. The time-dependent unperturbed Hamiltonian is taken as a TDHF including the complete basis set, in which the occupation number averages depend on time, according to how each of the one-particle states participates in the evolving many-body wavefunction. A perturbation expansion in terms of the two-particle residual interactions up to first order is subsequently carried out with great simplicity and transparency, giving rise to equations of motion for the Green functions in the Dyson-like form proposed by Keldysh [20]. The atomic charge-state fractions as functions of time are obtained from the two-particle correlation terms appearing in the differential Dyson equations that involve corrections in the residual interactions up to second order. This is an important goal of our work; the two-particle correlation functions at equal times are extracted from the solutions of the equations of motion, which in turn include the correlation effects in the evolution up to a

given particular time. This procedure provides a method to obtain the time dependence of atomic charge-state probabilities that goes beyond that of taking averages of the selected correlation functions over a state corrected up to an equivalent order in the perturbation.

On the other hand, as it is difficult to assess how well described are the correlation effects using these prescriptions, we have applied this method to the calculation of the charge-state probabilities for the time-dependent scattering of an atom by a three-level linear chain substrate [23] within an Anderson description, where comparisons with exact solutions [24] are possible. Although the ‘substrate’ size is in this case very limited so as to allow for extensive conclusions, we suggest that this technique can be advantageously used for various strengths of the interaction parameters, with results that compare fairly well with the exact values. Obviously, it would be highly desirable to use our proposal in conjunction with a more realistic and detailed description of the electronic states of the substrate [25, 26] to analyse their effects on the charge-transfer process. However, this is left for the future.

2. Theory

The electronic part of the Hamiltonian describing a system of interacting atoms can be written as the sum of two components:

$$H = H_F + H_I \quad (1)$$

where H_F is the one-particle Hamiltonian, the sum of operators representing the kinetic energy of the particles and their interaction with external sources (nuclei). The Hamiltonian H_I contains terms which represent the interactions between particles. Pair interaction is usually the most important. Introducing explicitly the spin index σ , the Hamiltonian implied by equation (1) can be written in second-quantized form as

$$H = \sum_{\mu\gamma\sigma} h_{\mu\gamma} A_{\mu\sigma}^+ A_{\gamma\sigma} + \frac{1}{4} \sum_{\lambda\eta\mu\gamma,\sigma} (V_{\eta\lambda\gamma\mu} - V_{\eta\lambda\mu\gamma}) A_{\eta\sigma}^+ A_{\lambda\sigma}^+ A_{\mu\sigma} A_{\gamma\sigma} + \frac{1}{2} \sum_{\lambda\eta\mu\gamma,\sigma} V_{\eta\lambda\gamma\mu} A_{\eta\sigma}^+ A_{\lambda-\sigma}^+ A_{\mu-\sigma} A_{\gamma\sigma} \quad (2)$$

where $A_{\gamma\sigma}^+$ and $A_{\gamma\sigma}$ are the fermion creation and annihilation operators associated with each single-particle state $X_{\gamma\sigma}$ of the complete set. The parameters in equation (2) are given by

$$h_{\mu\gamma} = \int dq X_{\mu}^*(q) h(q) X_{\gamma}(q)$$

$$V_{\eta\lambda\gamma\mu} = \int \int dq dq' X_{\eta}^*(q) X_{\lambda}^*(q') V(q, q') X_{\gamma}(q) X_{\mu}(q').$$

We are assuming that the interaction potential is spin independent and a function of only the particle coordinates. A starting point to an approximate solution of the Hamiltonian in equation (2) is provided by the one-particle effective Hamiltonian H_0 constructed by considering all possible averages of the pair interaction terms over a selected single determinant, this being the usual HF approximation to H . The residual H_p containing the two-particle interactions, obtained as the difference between the many-body Hamiltonian H and H_0 , may be treated within a perturbative scheme. H_0 is given by

$$H_0 = \sum_{\mu\nu\sigma} T_{\mu\nu}^{\sigma} A_{\mu\sigma}^+ A_{\nu\sigma} - \frac{1}{2} \sum_{\mu\nu\sigma} \{T_{\mu\nu}^{\sigma} - h_{\mu\nu}\} \langle A_{\mu\sigma}^+ A_{\nu\sigma} \rangle \quad (3)$$

with

$$T_{\mu\nu}^{\sigma} = h_{\mu\nu} + \sum_{\lambda\eta} \{V_{\mu\lambda\eta\nu} \langle A_{\lambda-\sigma}^+ A_{\eta-\sigma} \rangle + (V_{\mu\lambda\eta\nu} - V_{\lambda\mu\eta\nu}) \langle A_{\lambda\sigma}^+ A_{\eta\sigma} \rangle\}$$

and

$$H_p = H - H_0. \quad (4)$$

In time-dependent scattering processes in which the initial state corresponds to non-interacting subsystems, the probabilities of the charge-state configurations can be obtained from the averages of selected one- and two-particle operators taken at equal times. In order to include correlation effects in these calculations, we start with an unperturbed H_0 taken as a TDHF Hamiltonian with time-dependent occupation numbers, these varying from 0 to 1 at each time according to the probability of finding a particular one-particle state occupied in the determinant [27] that evolves as the interactions between the subsystems are turned on. If the one-particle states Φ_j are the eigenfunctions of $H_0(t)$ at the initial time $t = t_0$,

$$H_0(t_0)\Phi_j = \varepsilon_j \Phi_j$$

and the many-body eigenstate at t_0 is assumed to be a single determinant $\Psi_\alpha(t_0)$ constructed by filling a selected subset of the Φ_j states:

$$\Psi_\alpha(t_0) = \det\{\Phi_j\}_{j \in occ.in\alpha}.$$

The time evolution of the independent-particle wavefunction is

$$\Psi_\alpha(t) = \det\{U^{HF}(t, t_0)\Phi_j\}_{j \in occ.in\alpha}$$

where $U^{HF}(t, t_0)$ is the time evolution operator given by

$$U^{HF}(t, t_0) = T \exp \left\{ -i \int_{t_0}^t H_0(\tau) d\tau \right\}$$

and T is the chronological time-ordering operator. To calculate $\Psi(t)$, which solves the many-body dynamical problem

$$[H(t) - i\partial_t]\Psi(t) = 0 \quad (5)$$

one introduces the time evolution operator $U(t, t_0)$ for the full Hamiltonian $H(t)$ as

$$\Psi(t) = U(t, t_0)\Psi(t_0).$$

The operator $U(t, t_0)$ satisfies well known properties [28], and according to our selection it can be written in terms of $U^{HF}(t, t_0)$ and that part generated from the perturbation, which up to second order in H_p is given by

$$U(t, t_0) \approx U^{HF}(t, t_0) \left[1 - i \int_{t_0}^t d\tau \bar{H}_p(\tau) - \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \bar{H}_p(\tau_1) \bar{H}_p(\tau_2) \right]. \quad (6)$$

In equation (6), $\bar{H}_p(\tau)$ is defined as

$$\bar{H}_p(\tau) = U^{HF}(t_0, \tau) H_p(\tau) U^{HF}(\tau, t_0). \quad (7)$$

The expectation value at equal times of one- or two-particle correlation functions such as

$$\langle n_{\beta\sigma}(t) \rangle \equiv \langle A_{\beta\sigma}^+(t) A_{\beta\sigma}(t) \rangle \quad \langle n_{\beta\sigma}(t) n_{\beta-\sigma}(t) \rangle \equiv \langle A_{\beta\sigma}^+(t) A_{\beta\sigma}(t) A_{\beta-\sigma}^+(t) A_{\beta-\sigma}(t) \rangle$$

can be calculated using the relation between the Heisenberg $\langle O_H \rangle$ and the Schrödinger $\langle O_S \rangle$ pictures:

$$O_H(t) = U^+(t, t_0) O_S U(t, t_0).$$

Since these averages are taken over the state $U^{HF}(t, t_0)|\Psi(t_0)\rangle$, to get the first non-vanishing corrections to the TDHF one-particle correlation functions requires us to go to second order in H_p in equation (6), while first order in H_p gives the first non-zero corrections to the TDHF two-particle correlation functions. After some algebra, one finds that

$$\langle n_{\beta\sigma}(t) \rangle = \langle U(t_0, t)n_{\beta\sigma}U(t, t_0) \rangle \simeq \langle \bar{n}_{\beta\sigma}(t) \rangle - \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \langle [\bar{H}_p(\tau_2), [\bar{H}_p(\tau_1), \bar{n}_{\beta\sigma}(t)]] \rangle \quad (8)$$

and similarly

$$\langle n_{\beta\sigma}(t)n_{\beta-\sigma}(t) \rangle \simeq \langle \bar{n}_{\beta\sigma}(t) \rangle \langle \bar{n}_{\beta-\sigma}(t) \rangle - i \int_{t_0}^t d\tau \langle [\bar{n}_{\beta\sigma}(t)\bar{n}_{\beta-\sigma}(t), \bar{H}_p(\tau)] \rangle$$

where $[\dots, \dots]$ stands for the commutator and, as in equation (7), we have defined

$$\bar{O}_{\beta\sigma}(t) \equiv U^{HF}(t_0, t)O_{\beta\sigma}U^{HF}(t, t_0).$$

Thus, by assuming that the initial state $\Psi(t_0)$ is a HF eigenstate of $H_0(t_0)$, all averages are taken over a single-particle density matrix, with operators defined in an interaction picture referred to a TDHF system. By performing all the contractions as required by the Wick theorem, one finds that the perturbative corrections in equation (8) are all given in terms of TDHF averages. This procedure can also be applied to the case of two operators at different times, such as

$$\langle \bar{A}_{\beta\sigma}^+(t')\bar{A}_{\nu\sigma}(t) \rangle \quad \langle \bar{A}_{\nu\sigma}(t')\bar{A}_{\beta\sigma}^+(t) \rangle \quad \text{etc.}$$

In dynamical processes where several active configurations intervene, one is usually asked to find averages of selected strings of creation and annihilation operators taken at equal times [22]. The previous examples show a possible alternative to its calculation up to a given order of approximation, once perturbative corrections such as those in equation (8) are applied.

2.1. The Green functions, the equations of motion and the boundary conditions

Instead of the procedure outlined previously, we propose to take advantage of a more powerful formalism, based on the use of the time-dependent Green functions introduced by Keldysh [20], that goes beyond that implied by the calculation of expectation values as in equation (8). Defining

$$G_{\alpha\beta,\sigma}(t, t') = i \Theta(t' - t) \langle \Psi | \{A_{\beta\sigma}^+(t'), A_{\alpha\sigma}(t)\} | \Psi \rangle \quad (9)$$

and

$$F_{\alpha\beta\sigma}(t, t') = i \langle \Psi | [A_{\beta\sigma}^+(t'), A_{\alpha\sigma}(t)] | \Psi \rangle \quad (10)$$

where $|\Psi\rangle$ represents the initial (uncorrelated) state and $\{\dots, \dots\}$ refer to anticommutators. It is immediately seen that only the functions $F(t, t')$ taken at equal times determine the distribution of electrons and holes. The equations of motion for $G_{\xi\beta,\sigma}(t, t')$ and $F_{\xi\beta,\sigma}(t, t')$ are given by

$$\begin{aligned} i\partial_t G_{\xi\beta,\sigma}(t, t') &= \delta_{\xi\beta}\delta(t' - t) + \sum_{\nu} h_{\xi\nu} G_{\nu\beta,\sigma}(t, t') + \frac{1}{2}i\Theta(t' - t) \\ &\times \sum_{\alpha_1\alpha_2\alpha_3} (V_{\xi\alpha_3\alpha_1\alpha_2}(t) - V_{\alpha_3\xi\alpha_1\alpha_2}(t)) \langle \{A_{\beta\sigma}^+(t'), A_{\alpha_3\sigma}^+(t)A_{\alpha_1\sigma}(t)A_{\alpha_2\sigma}(t)\} \rangle \\ &+ i\Theta(t' - t) \sum_{\alpha_1\alpha_2\alpha_3} V_{\xi\alpha_3\alpha_1\alpha_2}(t) \langle \{A_{\beta\sigma}^+(t'), A_{\alpha_3-\sigma}^+(t)A_{\alpha_1-\sigma}(t)A_{\alpha_2\sigma}(t)\} \rangle \end{aligned}$$

and

$$\begin{aligned} i\partial_t F_{\xi\beta,\sigma}(t, t') &= \sum_{\nu} h_{\xi\nu} F_{\nu\beta,\sigma}(t, t') + \frac{1}{2}i \sum_{\alpha_1\alpha_2\alpha_3} (V_{\xi\alpha_3\alpha_1\alpha_2}(t) - V_{\alpha_3\xi\alpha_1\alpha_2}(t)) \\ &\quad \times \langle [A_{\beta\sigma}^+(t'), A_{\alpha_3\sigma}^+(t)A_{\alpha_1\sigma}(t)A_{\alpha_2\sigma}(t)] \rangle \\ &\quad + i \sum_{\alpha_1\alpha_2\alpha_3} V_{\xi\alpha_3\alpha_1\alpha_2}(t) \langle [A_{\beta\sigma}^+(t'), A_{\alpha_3-\sigma}^+(t)A_{\alpha_1-\sigma}(t)A_{\alpha_2\sigma}(t)] \rangle. \end{aligned}$$

The equations for the $G(t, t')$ are integrated from $t = t'$ with the boundary conditions

$$G_{\xi\beta,\sigma}(t', t') = i\delta_{\xi\beta}.$$

To solve the equations of motion for the $F(t, t')$ requires knowledge of the $F_{\xi\beta,\sigma}(t_0, t')$ as boundary conditions. If the ξ states are chosen as those which diagonalize the independent particle Hamiltonian $H_0(t_0)$ at $t = t_0$, for time values t' greater than t_0 we can calculate $F_{\xi\beta,\sigma}(t_0, t')$ as

$$F_{\xi\beta,\sigma}(t_0, t') = G_{\xi\beta,\sigma}(t_0, t')$$

for occupied ξ states and

$$F_{\xi\beta,\sigma}(t_0, t') = -G_{\xi\beta,\sigma}(t_0, t')$$

for empty ξ states. It is worth stressing that these last boundary conditions, as well as the application of the Wick theorem as used before and required in the following, strictly depend on an initial state described by an independent particle model (uncorrelated). If correlations in the initial state are important, the formalism should be modified so as to include these effects in the form given by Wagner [29]. In what follows we shall not consider this possibility.

To solve the equations of motion for the Green functions we approximate the two-particle interaction contributions by performing the perturbative expansion of equation (6) and retain terms up to first order in H_p . The explicit form for one of the possible averages generated by these terms can be written as

$$\begin{aligned} \langle A_{\beta\sigma}^+(t') A_{\alpha_3\sigma'}^+(t) A_{\alpha_1\sigma'}(t) A_{\alpha_2\sigma}(t) \rangle &\simeq \langle \bar{A}_{\beta\sigma}^+(t') \bar{A}_{\alpha_3\sigma'}^+(t) \bar{A}_{\alpha_1\sigma'}(t) \bar{A}_{\alpha_2\sigma}(t) \rangle \\ &\quad - i \int_{t_0}^{t'} d\tau \langle \bar{A}_{\beta\sigma}^+(t') [\bar{A}_{\alpha_3\sigma'}^+(t) \bar{A}_{\alpha_1\sigma'}(t) \bar{A}_{\alpha_2\sigma}(t), \bar{H}_p(\tau)] \rangle \\ &\quad - i \int_{t_0}^{t'} d\tau \langle [\bar{A}_{\beta\sigma}^+(t'), \bar{H}_p(\tau)] \bar{A}_{\alpha_3\sigma'}^+(t) \bar{A}_{\alpha_1\sigma'}(t) \bar{A}_{\alpha_2\sigma}(t) \rangle. \end{aligned} \quad (11)$$

After applying the contractions as required by the Wick theorem to one of the possible terms in equation (11) (for $\sigma = \sigma'$), one typically gets

$$\begin{aligned} \langle \bar{A}_{\beta\sigma}^+(t') \bar{A}_{\alpha_3\sigma}^+(t) \bar{A}_{\alpha_1\sigma}(t) \bar{A}_{\alpha_2\sigma}(t) \bar{H}_p(\tau) \rangle &= \sum_{\mu\nu\lambda\eta} (V_{\lambda\eta\mu\nu}(\tau) - V_{\eta\lambda\mu\nu}(\tau)) \langle \bar{A}_{\beta\sigma}^+(t') \bar{A}_{\nu\sigma}(\tau) \rangle \\ &\quad \times \langle \bar{A}_{\alpha_3\sigma}^+(t) \bar{A}_{\mu\sigma}(\tau) \rangle \langle \bar{A}_{\alpha_1\sigma}(t) \bar{A}_{\lambda\sigma}^+(\tau) \rangle \langle \bar{A}_{\alpha_2\sigma}(t) \bar{A}_{\eta\sigma}^+(\tau) \rangle. \end{aligned}$$

In this expression, which is of first order in H_p , one notices the presence of averages such as $\langle \bar{A}_{\beta\sigma}^+(t') \bar{A}_{\nu\sigma}(\tau) \rangle$ that strictly should be taken over operators referred to the TDHF representation. If these kinds of average are traced over all the two-particle contributions in the equations of motion, and if it is assumed that commutators or anticommutators as they appear are systematically replaced by say $F_{\xi\nu,\sigma}(\tau, t')$ and $G_{\xi\nu,\sigma}(t, t')$, respectively, this gives rise to Dyson-like equations that are of second order in H_p . Proceeding in this way, one arrives at the corrected form of the equations of motion, that can be written as

$$\begin{aligned} \partial_t G_{\xi\beta,\sigma}(t, t') &= -i\delta_{\xi\beta}\delta(t' - t) + (-i) \sum_{\mu} \{T_{\xi\mu}(t)G_{\mu\beta,\sigma}(t, t') \\ &+ \int_t^{t'} d\tau [\Xi_{\xi\mu,\sigma}^{a(J)}(t, \tau) + \Xi_{\xi\mu,\sigma}^{a(U)}(t, \tau)]G_{\mu,\beta,\sigma}(\tau, t')\} \end{aligned} \quad (12)$$

and

$$\begin{aligned} \partial_t F_{\xi\beta,\sigma}(t, t') &= (-i) \sum_{\mu} \left\{ T_{\xi\mu}(t)F_{\mu\beta,\sigma}(t, t') + \int_{t_0}^t d\tau [\Xi_{\xi\mu,\sigma}^{r(J)}(t, \tau) + \Xi_{\xi\mu,\sigma}^{r(U)}(t, \tau)]F_{\mu\beta,\sigma}(\tau, t') \right. \\ &\left. + \int_{t_0}^{t'} d\tau [\Omega_{\xi\mu,\sigma}^{(J)}(t, \tau) + \Omega_{\xi\mu,\sigma}^{(U)}(t, \tau)]G_{\mu\beta,\sigma}(\tau, t') \right\} \end{aligned} \quad (13)$$

where the explicit expressions for $\Xi_{\xi\mu,\sigma}^{r(J)}(t, \tau)$, $\Xi_{\xi\mu,\sigma}^{r(U)}(t, \tau)$, $\Omega_{\xi\mu,\sigma}^{(J)}(t, \tau)$ and $\Omega_{\xi\mu,\sigma}^{(U)}(t, \tau)$ are given in appendix 1. These functions are seen to be composed by strings of TDHF averages, in what it can be called an unrenormalized self-energy scheme [30]. Equations (12) and (13) represent the integrodifferential equations of motion in Dyson-like form, which allow us to correct the G and F functions by the residual part of the two-particle interactions terms, through the self-energy functions $\Xi_{\xi\mu,\sigma}^{r(J)}(t, \tau)$, $\Xi_{\xi\mu,\sigma}^{r(U)}(t, \tau)$, $\Omega_{\xi\mu,\sigma}^{(J)}(t, \tau)$ and $\Omega_{\xi\mu,\sigma}^{(U)}(t, \tau)$ that are of second order in these interactions. Thus, the time-dependent evolution requires us to solve the set of coupled equations (12) for the G , which are needed to solve equation (13) for the F , in a sort of iterative fashion, giving rise to an approximation that goes beyond second order. Note that, up to this order, terms corresponding to interactions between electrons with the same (superscript J) and opposite (superscript U) spin projections give separated contributions.

2.2. Expectation values of two-particle operators

Expectation values of two-particle operators taken at equal times can now be obtained from its corresponding contributions to the Dyson equation for $F(t, t')$ at $t = t'$. Using the same prescriptions leading to the construction of the self-energy terms in the equations of motion as in equation (A1.4), we can write for one of these contributions

$$\begin{aligned} i V_{\xi\alpha_3\alpha_1\alpha_2}(t) \langle [A_{\xi\sigma}^+(t), A_{\alpha_3-\sigma}^+(t)A_{\alpha_1-\sigma}(t)A_{\alpha_2\sigma}(t)] \rangle \\ \simeq V_{\xi\alpha_3\alpha_1\alpha_2}(t) \langle \bar{A}_{\alpha_3-\sigma}^+(t)\bar{A}_{\alpha_1-\sigma}(t)F_{\alpha_2\xi,\sigma}(t, t) \rangle \\ + \sum_{\mu} \int_{t_0}^t d\tau [\Xi_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{r(U)}(t, \tau)F_{\mu\xi,\sigma}(t, \tau) + \Omega_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{(U)}(t, \tau)G_{\mu\xi,\sigma}(t, \tau)]. \end{aligned}$$

By solving the commutator on the left-hand side, one finds that

$$\begin{aligned} \langle A_{\xi\sigma}^+(t)A_{\alpha_3-\sigma}^+(t)A_{\alpha_1-\sigma}(t)A_{\alpha_2\sigma}(t) \rangle &= \frac{1}{2} \left\{ \langle A_{\alpha_3-\sigma}^+(t)A_{\alpha_1-\sigma}(t) \rangle \delta_{\alpha_2\xi} - i \langle \bar{A}_{\alpha_3-\sigma}^+(t)\bar{A}_{\alpha_1-\sigma}(t) \rangle \right. \\ &\times F_{\alpha_2\xi,\sigma}(t, t) - \frac{i}{V_{\xi\alpha_3\alpha_1\alpha_2}(t)} \sum_{\mu} \int_{t_0}^t d\tau [\Xi_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{r(U)}(t, \tau)F_{\mu\xi,\sigma}(t, \tau) \\ &\left. + \Omega_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{(U)}(t, \tau)G_{\mu\xi,\sigma}(t, \tau) \right\} \end{aligned} \quad (14)$$

and, in a similar way as in equation (A1.3), we obtain for $V_{\xi\alpha_3\alpha_1\alpha_2}(t) \neq V_{\alpha_3\xi\alpha_1\alpha_2}(t)$

$$\begin{aligned} \langle A_{\xi\sigma}^+(t)A_{\alpha_3\sigma}^+(t)A_{\alpha_1\sigma}(t)A_{\alpha_2\sigma}(t) \rangle &= \frac{1}{2} \langle A_{\alpha_3\sigma}^+(t)A_{\alpha_1\sigma}(t) \rangle \delta_{\alpha_2\xi} - \frac{1}{2} \langle A_{\alpha_3\sigma}^+(t)A_{\alpha_2\sigma}(t) \rangle \delta_{\alpha_1\xi} \\ &- \frac{1}{2} i \langle \bar{A}_{\alpha_3\sigma}^+(t)\bar{A}_{\alpha_1\sigma}(t) \rangle F_{\alpha_2\xi,\sigma}(t, t) + \frac{1}{2} i \langle \bar{A}_{\alpha_3\sigma}^+(t)\bar{A}_{\alpha_2\sigma}(t) \rangle F_{\alpha_1\xi,\sigma}(t, t) \\ &- \frac{i}{V_{\xi\alpha_3\alpha_1\alpha_2}(t) - V_{\alpha_3\xi\alpha_1\alpha_2}(t)} \sum_{\mu} \int_{t_0}^t d\tau [\Xi_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{r(J)}(t, \tau)F_{\mu\xi,\sigma}(t, \tau) \\ &+ \Omega_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{(J)}(t, \tau)G_{\mu\xi,\sigma}(t, \tau)] \end{aligned} \quad (15)$$

where, according to equation (10),

$$\langle A_{\alpha_3\sigma}^+(t) A_{\alpha_1\sigma}(t) \rangle = [\delta_{\alpha_3\alpha_1} - i F_{\alpha_3\alpha_1,\sigma}(t, t)]/2$$

and $\Xi_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{r(U)}(t, \tau)$, $\Omega_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{(U)}(t, \tau)$, $\Xi_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{r(J)}(t, \tau)$ and $\Omega_{\xi\alpha_1\alpha_2\alpha_3\mu,\sigma}^{(J)}(t, \tau)$ are given explicitly in appendix 1. It is easy to check that, if the G and F functions in these equations were taken as their corresponding partners in the HF approximation, one returns to the prescription leading to expressions such as those in equation (8). Equations (14) and (15) summarize our proposal for the calculation of the charge-state configurations in a dynamical process, when two-particle interactions are involved. This goes beyond the TDHF scheme and provides a better approximation than that represented by equation (8), because of the continuous feedback in time required to solve equations (12) and (13) as $t \rightarrow t'$.

2.3. Analysis on the applicability of this formalism

Equations (14) and (15) provide a transparent way to calculate the probabilities for different charge configurations in dynamical collision processes. To visualize the scope of this method, let us assume two colliding systems, which may consist of an ion or an atom and a cluster of atoms. In this case and at large separations the ξ states run over the eigenstates of each subsystem. If there are N_1 states describing one of them, and N_2 describing the other, the calculation of the correlated Green functions $G_{\xi\beta,\sigma}(t, t')$ and $F_{\xi\beta,\sigma}(t, t')$ requires us to solve two sets of $N_1 \times N_2$ integrodifferential equations at each time t evolving from or to t' . Previously, it is necessary to solve the $N_1 \times N_2$ differential equations leading to the TDHF Green functions which define the self-energy functions $\Xi_{\xi\mu,\sigma}(t, \tau)$ and $\Omega_{\xi\mu,\sigma}(t, \tau)$. As it appears, the whole procedure seems to imply an almost impossible task for large systems. However, we would like to point out that this calculation is focused on the corrections introduced by the all two-particle interaction terms appearing in the many-body Hamiltonian (2). This may not represent an insurmountable difficulty, particularly if one assumes a pair-bond interaction model [31, 32] for equation (2), which reduces the number of the two-particle terms to those having no more than three different state indexes. From this picture, one can in addition retain only those two-particle interaction terms that are crucial for the process of interest, to be treated beyond the TDHF approximation. This is the situation when an Anderson description of an atom–surface collisional process is used. In this case, only the electronic repulsion at the adatom site is taken into account, as this is assumed to be the most important two-body ingredient in fixing the asymptotic charge-state probabilities for the scattered atom.

3. Ion (or atom) scattering from a solid surface within a time-dependent Anderson model

In its simplest version the Anderson Hamiltonian describing a collisional process can be written as

$$H(t) = \varepsilon_a \sum_{\sigma} n_{a\sigma} + U n_{a\uparrow} n_{a\downarrow} + \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{k\sigma} (V_{ka}(t) A_{k\sigma}^+ A_{a\sigma} + V_{ak}(t) A_{a\sigma}^+ A_{k\sigma})$$

where the notation is standard and $V_{ka}(t)$ is a time-dependent hopping parameter describing the interaction between the atomic a and the k states of the substrate. The time dependence of V_{ka} is attributed to the motion of the scattered particle along a classical trajectory and can be taken as

$$V_{ka}(t) = V_{ak}^*(t) = V_{ka} \exp(-\lambda|t|) \quad \text{with } \lambda = \lambda_0 v$$

where λ_0^{-1} is the decaying length of the interaction and v is the velocity (assumed constant along the trajectory) of the incoming particle. In this case, the TDHF leads to

$$H(t) = \sum_{\sigma} (\varepsilon_a + U \langle \bar{n}_{a-\sigma}(t) \rangle) n_{a\sigma} + \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{k\sigma} V_{ka}(t) (A_{k\sigma}^+ A_{a\sigma} + A_{a\sigma}^+ A_{k\sigma}) - U \langle \bar{n}_{a\uparrow}(t) \rangle \langle \bar{n}_{a\downarrow}(t) \rangle + H_p$$

with the perturbation term H_p given by

$$H_p(t) = U [n_{a\uparrow} - \langle \bar{n}_{a\uparrow}(t) \rangle] [n_{a\downarrow} - \langle \bar{n}_{a\downarrow}(t) \rangle]$$

where $\langle \bar{n}_{a\sigma}(t) \rangle$ means a TDHF average. The probabilities for the different charge states of the scattered particle, which is assumed neutral when it has one electron, are obtained from

$$\begin{aligned} P^-(t) &= \langle n_{a\uparrow}(t) n_{a\downarrow}(t) \rangle \\ P^0(t) &= \langle n_{a\uparrow}(t) \rangle + \langle n_{a\downarrow}(t) \rangle - 2 \langle n_{a\uparrow}(t) n_{a\downarrow}(t) \rangle \\ P^+(t) &= 1 - P^0(t) - P^-(t) \end{aligned}$$

where P^- , P^0 and P^+ represent the charge-state probabilities for negative, neutral and positive situations, respectively. In this particular case, knowledge of $\langle n_{a\sigma}(t) \rangle$ and $\langle n_{a\uparrow}(t) n_{a\downarrow}(t) \rangle$ determine the probabilities of all possible states of charge for the scattered particle.

3.1. Time-dependent Hartree–Fock solution

Introducing the one-particle Green functions

$$G_{aq,\sigma}^0(t, t_0) = i \Theta(t - t_0) \langle \{ \bar{A}_{q\sigma}^+(t_0), \bar{A}_{a\sigma}(t) \} \rangle$$

where $\bar{A}_{q\sigma}^+(t_0)$ creates an electron in an eigenstate q of the $H_0(t)$ at the initial time t_0 . In the atom–solid scattering process the q states run over the complete set of states: the atomic a and the solid k states. These Green functions are calculated by solving the equations of motion

$$\partial_t G_{aq,\sigma}^0(t, t_0) = -i \{ i \Theta(t - t_0) \langle \{ \bar{A}_{q\sigma}^+(t_0), [\bar{A}_{a\sigma}(t), H_0(t)] \} \rangle - \delta(t - t_0) \delta_{qa} \}$$

which have been discussed in previous work [33, 34]. The occupation number at the atomic site is obtained as

$$\langle \bar{n}_{a\sigma}(t) \rangle = \sum_{q \in \text{occupied}} |G_{aq,\sigma}^0(t, t_0)|^2$$

where the sum runs over the initially occupied eigenstates of H_0 . Within the TDHF approximation, the probability for a negatively charged particle reduces to

$$P^-(t) = \langle \bar{n}_{a\uparrow}(t) \rangle \langle \bar{n}_{a\downarrow}(t) \rangle.$$

3.2. The Dyson-like equations of motion for the Green functions

The Green functions associated with the full Hamiltonian $H(t)$ introduced in this case are

$$g_{qa,\sigma}(t, t') = i \Theta(t' - t) \langle \{ A_{a\sigma}^+(t'), A_{q\sigma}(t) \} \rangle \exp \left(-i \int_{t'}^t d\tau \varepsilon_q^\sigma(\tau) \right) \quad (16)$$

and

$$f_{qa,\sigma}(t, t') = i \langle [A_{a\sigma}^+(t'), A_{q\sigma}(t)] \rangle \exp \left(-i \int_{t'}^t d\tau \varepsilon_q^\sigma(\tau) \right) \quad (17)$$

with

$$\varepsilon_q^\sigma(\tau) = \begin{cases} \varepsilon_a + U \langle \bar{n}_{a-\sigma}(\tau) \rangle & q = a \\ \varepsilon_k & q = k \neq a. \end{cases}$$

To get the equations of motion for $g_{aa,\sigma}(t, t')$ and $f_{aa,\sigma}(t, t')$ in a closed form require knowledge of $g_{ak,\sigma}(t, t')$ and $f_{ak,\sigma}(t, t')$, which can be obtained by integration of its corresponding equations of motion obtained from equations (16) and (17), respectively. Applying the same prescriptions leading to equations (12) and (13), one arrives at

$$\partial_t g_{aa,\sigma}(t, t') = -i \left\{ \int_t^{t'} d\tau [\tilde{\Xi}_\sigma^{a(V)}(t, \tau) + \tilde{\Xi}_\sigma^{a(U)}(t, \tau)] g_{aa,\sigma}(\tau, t') + \delta(t - t') \right\} \quad (18)$$

$$\begin{aligned} \partial_t f_{aa,\sigma}(t, t') = & -i \left\{ \int_{t_0}^t d\tau [\tilde{\Xi}_\sigma^{r(V)}(t, \tau) + \tilde{\Xi}_\sigma^{r(U)}(t, \tau)] f_{aa,\sigma}(\tau, t') \right. \\ & \left. + \int_{t_0}^{t'} d\tau [\tilde{\Omega}_\sigma^{(V)}(t, \tau) + \tilde{\Omega}_\sigma^{(U)}(t, \tau)] g_{aa,\sigma}(\tau, t') \right\}. \end{aligned} \quad (19)$$

In obtaining the final expression of $\partial_t f_{aa,\sigma}(t, t')$ we have used the boundary conditions

$$f_{qa,\sigma}(t_0, t') = \begin{cases} g_{qa,\sigma}(t_0, t') & q_\sigma \in \text{occupied at } t = t_0 < t' \\ -g_{qa,\sigma}(t_0, t') & q_\sigma \in \text{empty at } t = t_0 < t'. \end{cases}$$

The functions $\tilde{\Xi}$ and $\tilde{\Omega}$ appearing in equations (18) and (19) are given explicitly in appendix 2.

The average occupation number at the scattered atom site is given by

$$\langle n_{a\sigma}(t) \rangle = \frac{1}{2} [1 - i f_{aa,\sigma}(t, t)] \quad (20)$$

and, according to equation (14), the probability of a negative charged state is obtained as

$$\begin{aligned} P^-(t) = & \frac{1}{2} \left\{ \langle n_{a\sigma}(t) \rangle - i \langle \bar{n}_{a-\sigma}(t) \rangle f_{aa,\sigma}(t, t) \right. \\ & \left. - \frac{i}{U} \int_{t_0}^t d\tau [\tilde{\Xi}_\sigma^{r(U)}(t, \tau) f_{aa,\sigma}(\tau, t) + \tilde{\Omega}_\sigma^{(U)}(\tau, t) g_{aa,\sigma}(\tau, t)] \right\}. \end{aligned} \quad (21)$$

3.3. Perturbative corrections applied over time-dependent Hartree–Fock averages at equal times

According to equations (8) and (11), including the first non-vanishing corrections to the HF $\langle n_{a\sigma}(t) \rangle$ and $\langle n_{a\uparrow}(t) n_{a\downarrow}(t) \rangle$ averages, we obtain

$$\begin{aligned} \langle n_{a\sigma}(t) \rangle = & \langle \bar{n}_{a\sigma}(t) \rangle + 2\text{Re} \left\{ U^2 \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 [\langle \{\bar{A}_{a\sigma}^+(t), \bar{A}_{a\sigma}(\tau_1)\} \rangle \langle \bar{A}_{a\sigma}^+(\tau_1) \bar{A}_{a\sigma}(\tau_2) \rangle \right. \\ & \times \langle \bar{A}_{a\sigma}(t) \bar{A}_{a\sigma}^+(\tau_2) \rangle - \langle \{\bar{A}_{a\sigma}^+(\tau_1), \bar{A}_{a\sigma}(t)\} \rangle \langle \bar{A}_{a\sigma}(\tau_1) \bar{A}_{a\sigma}^+(\tau_2) \rangle \langle \bar{A}_{a\sigma}^+(t) \bar{A}_{a\sigma}(\tau_2) \rangle] \\ & \left. \times \langle \bar{A}_{a-\sigma}^+(\tau_1) \bar{A}_{a-\sigma}(\tau_2) \rangle \langle \bar{A}_{a-\sigma}(\tau_1) \bar{A}_{a-\sigma}^+(\tau_2) \rangle \right\} \end{aligned} \quad (22)$$

and

$$\begin{aligned} \langle n_{a\uparrow}(t) n_{a\downarrow}(t) \rangle = & \langle \bar{n}_{a\uparrow}(t) \rangle \langle \bar{n}_{a\downarrow}(t) \rangle - 2U \\ & \times \text{Im} \int_{t_0}^t d\tau \langle \bar{A}_{a\uparrow}(\tau) \bar{A}_{a\uparrow}^+(\tau) \rangle \langle \bar{A}_{a\uparrow}^+(\tau) \bar{A}_{a\uparrow}(\tau) \rangle \langle \bar{A}_{a\downarrow}(\tau) \bar{A}_{a\downarrow}^+(\tau) \rangle \langle \bar{A}_{a\downarrow}^+(\tau) \bar{A}_{a\downarrow}(\tau) \rangle \end{aligned} \quad (23)$$

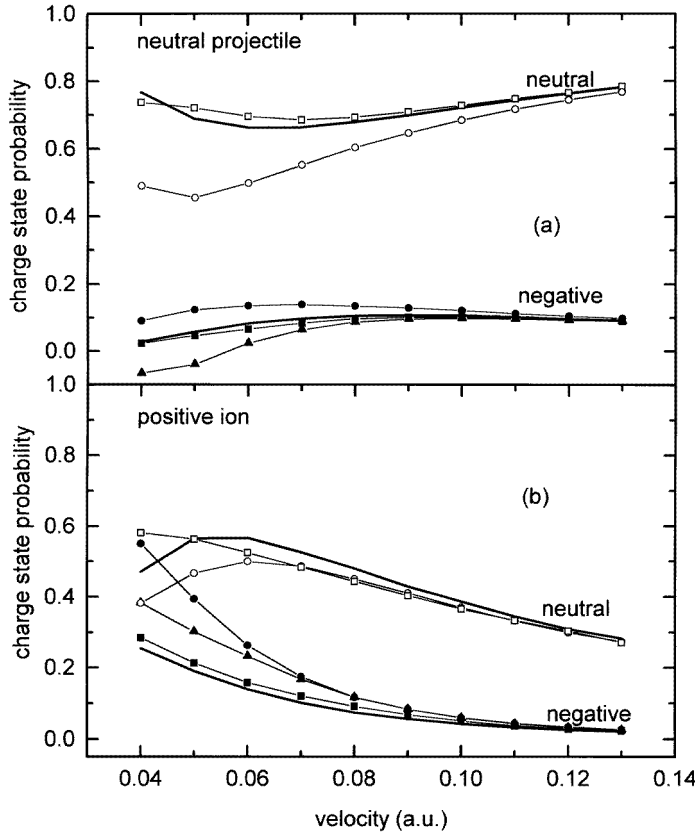


Figure 1. Probabilities P^0 and P^- of charge states for the scattered particle versus velocity with $U = 2$ eV and $\varepsilon_a = -0.5$ eV for (a) an incoming neutral particle and (b) an incoming positive ion: \circ , \bullet , TDHF results; \square , \blacksquare , obtained according to equations (20) and (21) in the text; —, exact results; \blacktriangle , TDHF plus corrections as in equation (23).

where the TDHF averages at different times are calculated using the identities [33]

$$\begin{aligned} \langle \bar{A}_{a\sigma}^+(\tau) \bar{A}_{a\sigma}(t) \rangle &= \sum_{qocc} G_{aq,\sigma}^{0*}(\tau, t_0) G_{aq,\sigma}^0(t, t_0) \\ \langle \bar{A}_{a\sigma}(t) \bar{A}_{a\sigma}^+(\tau) \rangle &= \sum_{qempty} G_{aq,\sigma}^{0*}(\tau, t_0) G_{aq,\sigma}^0(t, t_0). \end{aligned} \quad (24)$$

3.4. Application of the method: scattering of an atom (ion) by a three-level substrate

Our model system consists of a chain of four atoms [23], one representing the scattered particle and the other three the solid substrate. The three-atom substrate accounts for an incipient solid band formation and allows for an exact treatment of the dynamical charge exchange between the projectile and this discrete surface. This simplified model permits us to test the accuracy of our proposal against the well known limitations of the TDHF [17], and against that obtained by a second-order perturbative treatment as in equation (8). It is obvious that this model system will exhibit features in its velocity and U -dependence that are characteristic of a discrete-level system [34, 35]. However, we do not expect that

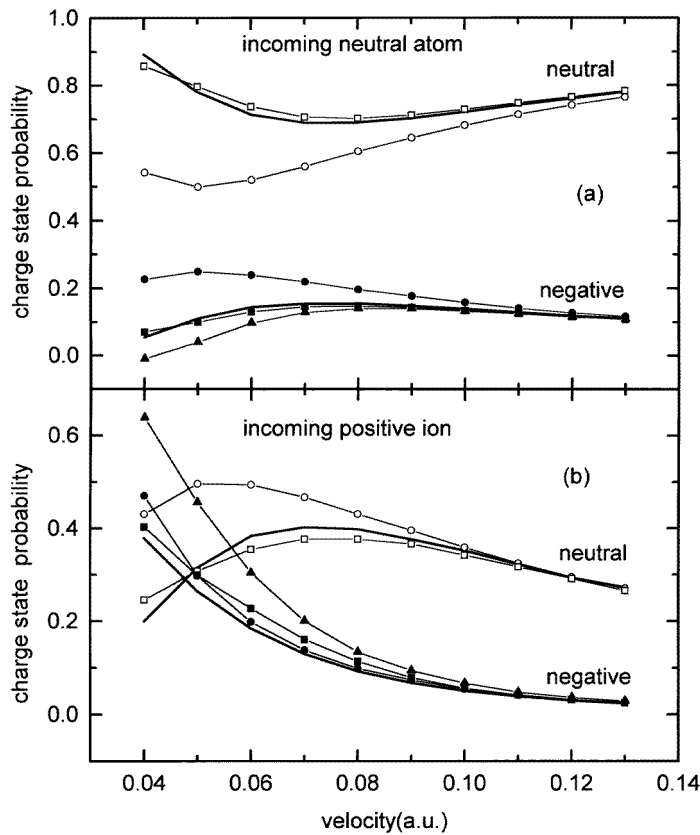


Figure 2. Probabilities P^0 and P^- of charge states for the scattered particle versus velocity with $U = 2$ eV, and $\varepsilon_a = -1$ eV for (a) an incoming neutral particle and (b) an incoming positive ion: \circ , \bullet , TDHF results; \square , \blacksquare , obtained according to equations (20) and (21) in the text; — exact results; \blacktriangle , TDHF plus corrections as in equation (23).

the general conclusions obtained from our proposal become invalid when a more realistic description of the substrate states is adopted. For the case of a finite band width involving a quasi-continuous set of states the calculation will require a manageable number of k states (about 30–40) while, for an infinite band width, the calculation simplifies because of the analytical expressions that one gets in the TDHF stage.

4. Results and discussion

In all cases we have taken $\lambda_0 = 2 \text{ \AA}^{-1}$ and $V_{ak} = -1$ eV. For the three-atom linear substrate the atom–atom hopping interaction $\beta = -2$ eV, and the site energy $\varepsilon_0 = 0$ eV. Two initial charge-state configurations of the incoming particle have been examined.

- (i) The incoming particle is neutral, which implies one electron in the atomic level and the other three in the substrate.
- (ii) The incoming particle is a positive ion, while four electrons are localized on the three-atom substrate.

The exact solutions were obtained by solving the time-dependent Anderson Hamiltonian

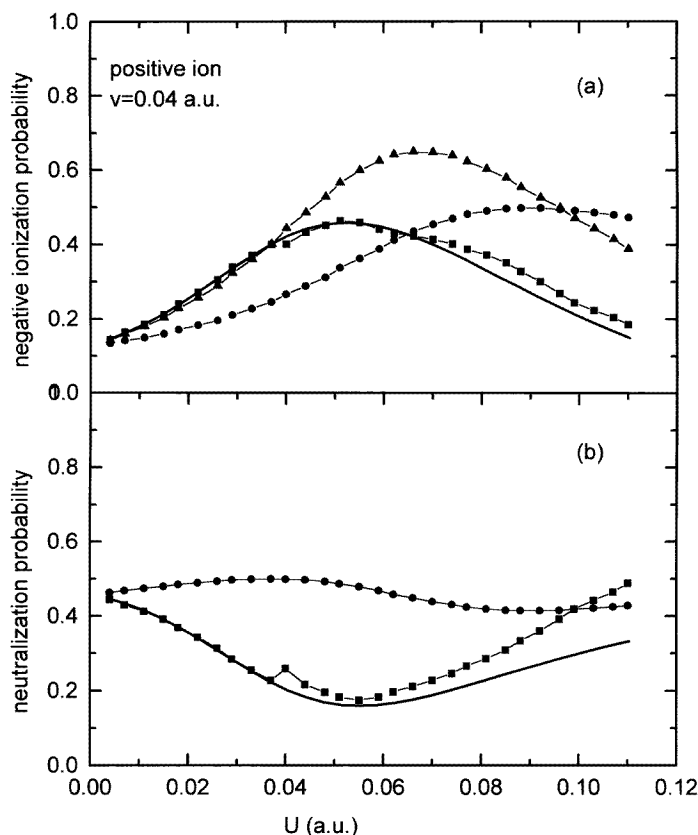


Figure 3. Probabilities (a) P^- and (b) P^0 of charge states for a scattered incoming ion as functions of U with $v = 0.04$ au and $\varepsilon_a = -1$ eV: ●, TDHF results; ■, obtained according to equations (20) and (21) in the text; —, exact results; ▲, TDHF plus corrections as in equation (23).

within the subspace of 36 many-body determinants [24] with $S_z = 0$, in either case. Results for the asymptotic negative and neutral charge-state probabilities as a function of the atom velocity and of the correlation parameter U are given. Comparisons of P^- obtained from equation (21) with the TDHF and the exact solutions are presented in each case. Results for P^- obtained from equation (23) are also included. The evolution of these probabilities with time is also shown.

4.1. Velocity dependence of the charge-transfer probabilities

In figures 1 and 2 we can see for two different values of ε_a the probabilities of neutral and negative final charge states of the scattered particle, for the two situations analysed: firstly an incoming neutral atom, and secondly an incoming positive ion. Our results, based on equation (21) are very satisfactory in a wide range of velocity values.

For a neutral projectile the results seem to be better than in the case of an ionic projectile, possibly because in the first case the calculation is based on an unrestricted TDHF, while in the second this is necessarily a restricted TDHF calculation as $\langle n_{a\uparrow}(t_0) \rangle = \langle n_{a\downarrow}(t_0) \rangle = 0$. We can see that all calculations are coincident at large velocities. This result can be understood

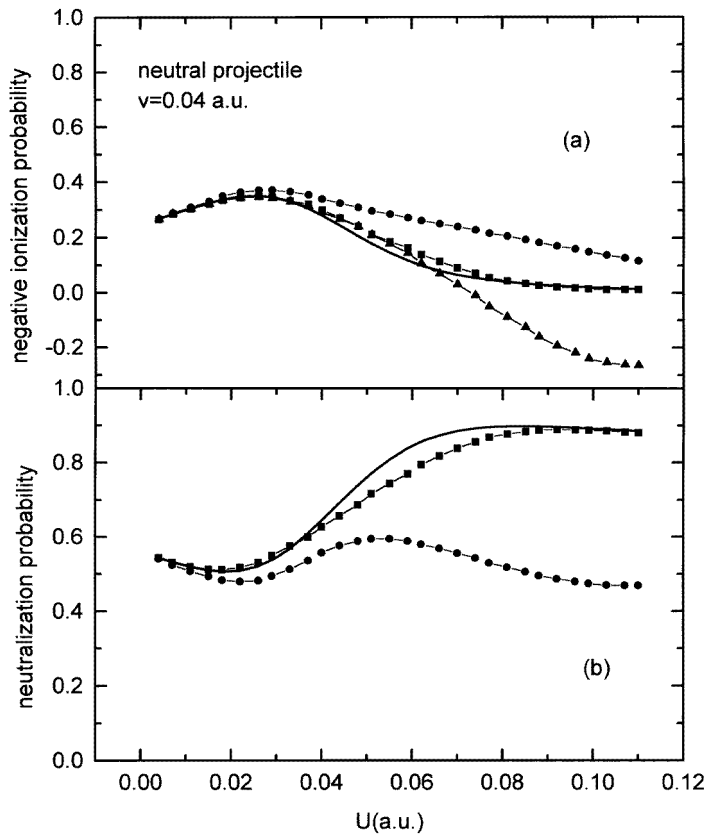


Figure 4. Probabilities (a) P^- and (b) P^0 of charge states for a scattered incoming neutral atom as functions of U with $v = 0.04$ au and $\varepsilon_a = -1$ eV: \bullet , TDHF results; \blacksquare , obtained according to equations (20) and (21) in the text; — , exact results; \blacktriangle , TDHF plus corrections as in equation (23).

by taking into account the uncertainty in energy of the atomic level introduced by the finite projectile velocity. In atomic units this energy uncertainty δE is of the order of the velocity v [36]. If within this δE the ionization and affinity levels are not clearly separated, a restricted TDHF calculation based on an ‘effective’ single-electron level is expected to produce reasonable results. This situation is reached for velocities larger than the U -value ($v \gg 0.7$ au) which means that $\delta E \gg U$, as seen from these figures. For a neutral incoming particle the situation is not so clear since the unrestricted TDHF leads to the existence of two different effective one-electron levels depending on the spin projections. In this case the TDHF results approach more slowly the exact results at large velocities.

We can also observe that P^- as obtained from equation (23) fails at small velocities, and it can produce unphysical results such as negative values of the probabilities in the case of an unrestricted TDHF zeroth-order solution. This is in contrast with our Green functions calculation, giving results that are in better agreement with the exact values when based on an unrestricted TDHF. At this point it should be stressed that the use of equation (21) or (23) to obtain P^- represents in fact different degrees of approximations in H_p . Thus, while P^- is given in terms of the Green functions by equation (21) whose equations of motion have

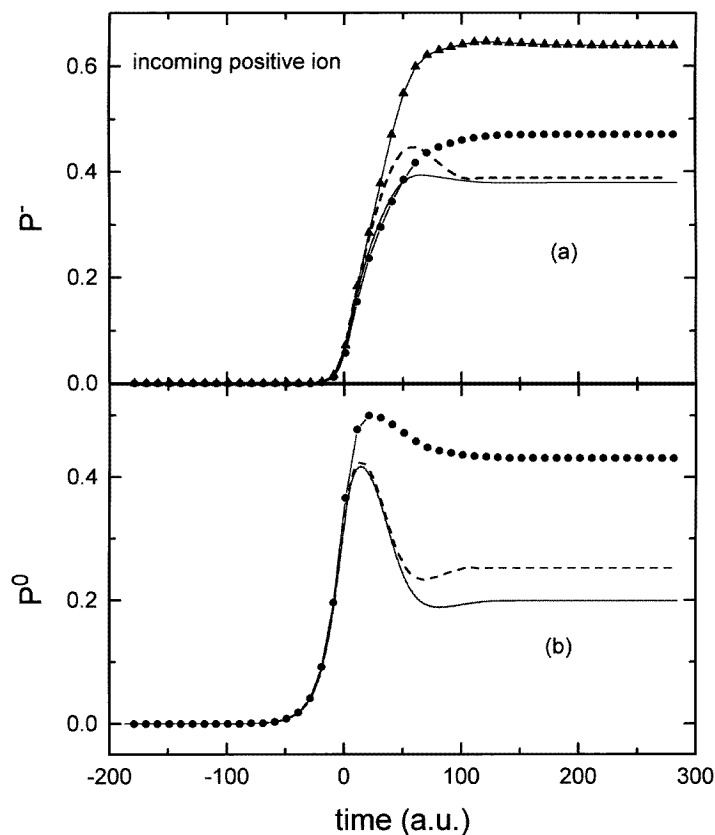


Figure 5. Probabilities (a) P^- and (b) P^0 of charge states for a scattered incoming ion as functions of time with $U = 2$ eV, $v = 0.04$ au and $\varepsilon_a = -1$ eV: ●, TDHF results; ---, obtained according to equations (20) and (21) in the text; —, exact results; ▲, TDHF plus corrections as in equation (23).

been corrected up to second order in H_p , equation (23) involves only the first non-vanishing contributions to the TDHF values of P^- , which is only of first order in the perturbation. Of course, it would be possible to add higher-order corrections in H_p to equation (23) (in particular second-order corrections to $\langle n_{a\uparrow}(t)n_{a\downarrow}(t) \rangle$ do not vanish), although it appears that this effort can be avoided in view of our results. On the other hand, perturbative corrections such as those leading to equation (23) may not guarantee a good rate of convergence. In addition, in the equations of motion for the Green functions the memory effects of the corrections are updated as $t \rightarrow t'$ by contrast with those in equation (23), where the whole memory of the process is contained only within the TDHF approximation of the evolution operator.

4.2. U dependence of the charge-transfer probability

Figures 3 and 4 show remarkable agreement between our results and the exact results for a wide range of U -values, even at the smallest velocity value ($v = 0.04$ au). The substantial improvement introduced by our method can be appreciated from these figures with respect to both the TDHF and those obtained from equation (23). In particular these last calculations

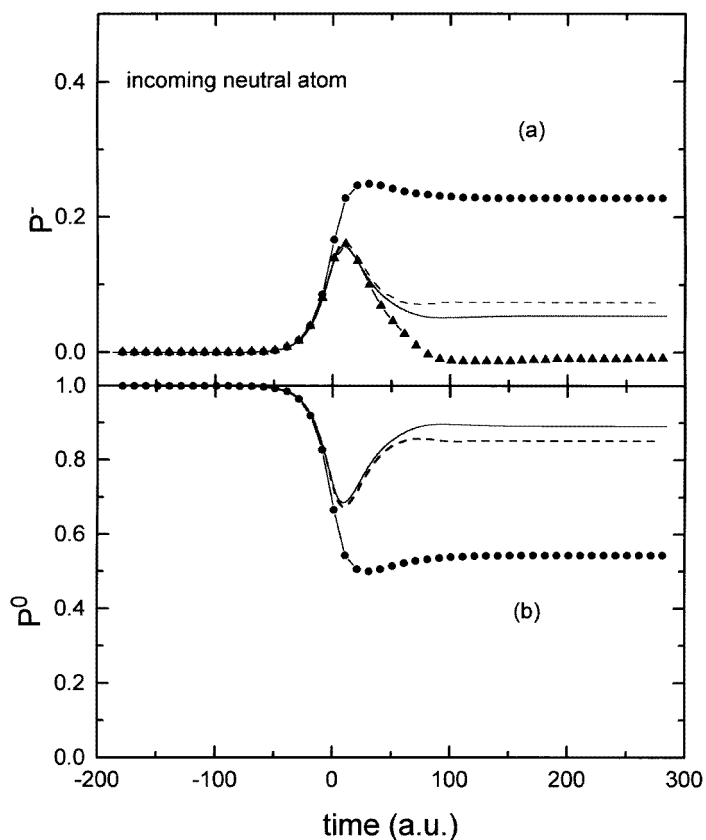


Figure 6. Probabilities (a) P^- and (b) P^0 of charge states for a scattered incoming neutral atom as functions of time with $U = 2$ eV, $v = 0.04$ au and $\varepsilon_a = -1$ eV: \bullet , TDHF results; $---$, obtained according to equations (20) and (21) in the text; $—$, exact results; \blacktriangle , TDHF plus corrections as in equation (23).

give poor results for large values of U compared with the energy uncertainty which is of the order of the velocity (in this case $v = 0.04$ au). Negative values of the probability are also obtained by using equation (23) for large values of U when the incoming particle is neutral.

4.3. Time dependence of the charge-transfer probability

In figures 5 and 6 we can see that our results, based on the calculation of $F(t, t')$ at each instant of time, in terms of the evolution up to $t' \rightarrow t$ corrected by correlation effects, are in very good agreement with the exact time variation. We can also observe that the TDHF approximation works reasonably well when the projectile approaches the ‘surface’, but it fails in describing the outgoing part of the trajectory. This is in agreement with the results obtained by Sebastian [17] using the CCA.

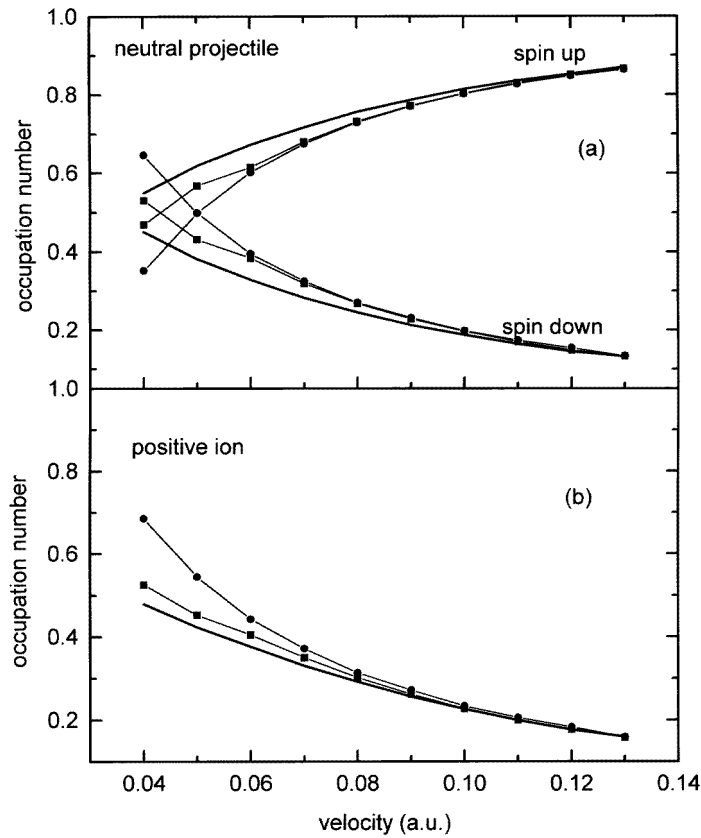


Figure 7. Occupation numbers $\langle n_{a\sigma}(\infty) \rangle$ for (a) an incoming neutral atom and (b) an incoming ion as functions of velocity with $U = 2$ eV and $\varepsilon_a = -1$ eV; \bullet , TDHF results; \blacksquare , obtained according to equation (20) in the text; —, exact results.

4.4. Occupation number as a function of velocity and the correlation parameter

Figures 7 and 8 show the velocity and U dependences, respectively, of the occupation numbers for the neutral (figures 7(a) and 8(a)) and ionic (figures 7(b) and 8(b)) projectile cases, obtained using the iterative feedback along the time evolution. We can observe very good agreement with the exact results at large values of U and small velocities, where the correlation effects are expected to be significant. In summary, our proposal to deal with the effects of the electronic interaction on time-dependent correlation functions (equations (14) and (15)) produce results in very good agreement with those obtained by the exact calculation within an ample range of velocities and U -values. This represents a substantial improvement over the TDHF and that of performing a second-order correction on the required matrix elements, which is expected to persist even when a more realistic description of the solid target is adopted.

4.5. Advantages with respect to the coupled-cluster approach

In comparing the capabilities of our method with that proposed by Sebastian [17] we can note the following.

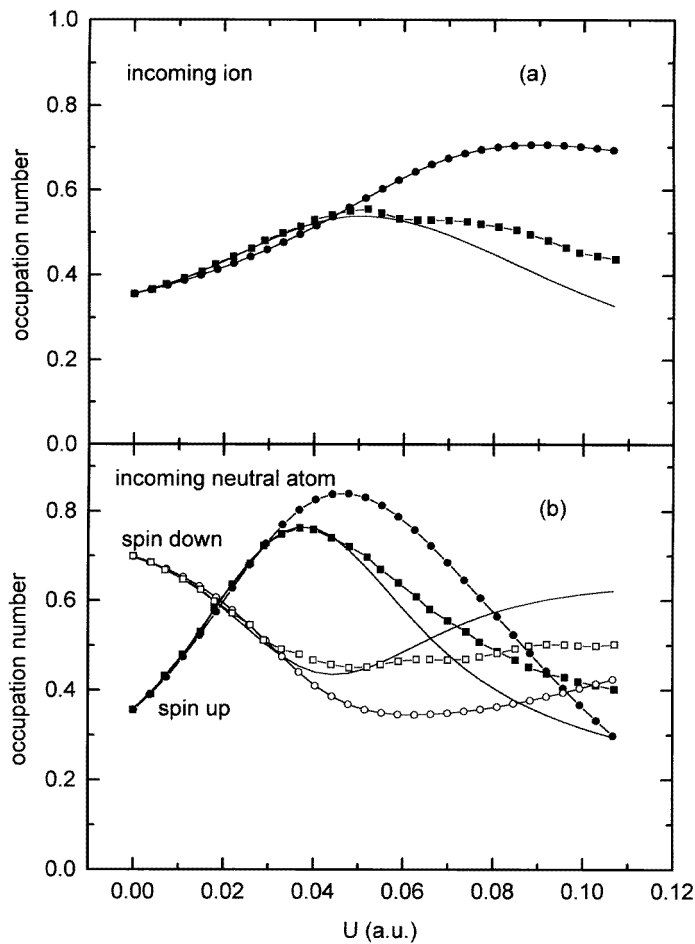


Figure 8. Occupation numbers $\langle n_{a\sigma}(\infty) \rangle$ for (a) an incoming ion and (b) an incoming neutral atom as functions of U with $v = 0.04$ au and $\varepsilon_a = -1$ eV: \circ , \bullet , TDHF results; \square , \blacksquare : obtained according to equation (20) in the text; —, exact results. In (b) the open and full symbols correspond to results for spin down and spin up, respectively.

(i) Within the CCA there is no efficient way to compute the expectation values of the operators of interest [17], while our proposal (equations (14) and (15)) accounts for a transparent and straightforward calculation of these expectation values.

(ii) We have no problems related to the truncation of expressions which affects the normalization as is the case of Sebastian's treatment (equation 12 in [17]). Our time-dependent correlated system is expanded in the complete set of TDHF wavefunctions, and the self-consistent solutions of Dyson-like equations (12) and (13) ensure the proper normalization requirements.

(iii) To obtain the Green functions within the TDHF approximation we have to solve N differential equations, where N is the total number of k states. For a semi-infinite three-dimensional solid, one needs three quantum numbers (k_x, k_y, k_z) to specify a given orbital of the solid. Considering for instance ten k -points, this implies 10^3 differential equations. There is no doubt that this represents a difficult numerical job, but we have 10^3 differential

equations less than in the case of the CCA for the same situation [17]. However, for a one-dimensional substrate the number of equations reduces to ten in our formalism as against 10^2 in the CCA. The correlated $g_{aa,\sigma}(t, t')$ and $f_{aa,\sigma}(t, t')$ Green functions required in this case imply solving an integrodifferential equation for each of them (equations (18) and (19)).

Acknowledgments

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Appendix 1

Following the prescriptions described in the text, the two-particle contributions to the equations of motion of the G and F functions, these can be written as follows.

A1.1 The equations of motion of G

$$\begin{aligned}
 i \Theta(t' - t) \sum_{\alpha_1 \alpha_2 \alpha_3} \frac{1}{2} (V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) - V_{\alpha_3 \xi \alpha_1 \alpha_2}(t)) & \langle \{A_{\beta \sigma}^+(t'), A_{\alpha_3 \sigma}^+(t) A_{\alpha_1 \sigma}(t) A_{\alpha_2 \sigma}(t)\} \rangle \\
 & = \sum_{\alpha_1 \alpha_2 \alpha_3} \left\{ (V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) - V_{\alpha_3 \xi \alpha_1 \alpha_2}(t)) \langle \bar{A}_{\alpha_3 \sigma}^+(t) \bar{A}_{\alpha_1 \sigma}(t) \rangle G_{\alpha_2 \beta, \sigma}(t, t') \right. \\
 & \quad \left. + \sum_{\mu} \int_t^{t'} d\tau \Xi_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{a(J)}(t, \tau) G_{\mu \beta, \sigma}(\tau, t') \right\} \quad (A1.1)
 \end{aligned}$$

$$\begin{aligned}
 i \Theta(t' - t) \sum_{\alpha_1 \alpha_2 \alpha_3} V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) & \langle \{A_{\beta \sigma}^+(t'), A_{\alpha_3 - \sigma}^+(t) A_{\alpha_1 - \sigma}(t) A_{\alpha_2 \sigma}(t)\} \rangle \\
 & = \sum_{\alpha_1 \alpha_2 \alpha_3} \left\{ V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) \langle \bar{A}_{\alpha_3 - \sigma}^+(t) \bar{A}_{\alpha_1 - \sigma}(t) \rangle G_{\alpha_2 \beta, \sigma}(t, t') \right. \\
 & \quad \left. + \sum_{\mu} \int_t^{t'} d\tau \Xi_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{a(U)}(t, \tau) G_{\mu \beta, \sigma}(\tau, t') \right\}. \quad (A1.2)
 \end{aligned}$$

A1.2 The equations of motion of F

$$\begin{aligned}
 i \sum_{\alpha_1 \alpha_2 \alpha_3} \frac{1}{2} (V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) - V_{\alpha_3 \xi \alpha_1 \alpha_2}(t)) & \langle [A_{\beta \sigma}^+(t'), A_{\alpha_3 \sigma}^+(t) A_{\alpha_1 \sigma}(t) A_{\alpha_2 \sigma}(t)] \rangle \\
 & = \sum_{\alpha_1 \alpha_2 \alpha_3} \left\{ (V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) - V_{\alpha_3 \xi \alpha_1 \alpha_2}(t)) \langle \bar{A}_{\alpha_3 \sigma}^+(t) \bar{A}_{\alpha_1 \sigma}(t) \rangle F_{\alpha_2 \beta, \sigma}(t, t') \right. \\
 & \quad + \sum_{\mu} \int_{t_0}^t d\tau \Xi_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{r(J)}(t, \tau) F_{\mu \beta, \sigma}(\tau, t') \\
 & \quad \left. + \sum_{\mu} \int_{t_0}^{t'} d\tau \Omega_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{(J)}(t, \tau) G_{\mu \beta, \sigma}(\tau, t') \right\} \quad (A1.3)
 \end{aligned}$$

$$\begin{aligned}
& i \sum_{\alpha_1 \alpha_2 \alpha_3} [V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) \langle [A_{\beta \sigma}^+(t'), A_{\alpha_3 - \sigma}^+(t) A_{\alpha_1 - \sigma}(t) A_{\alpha_2 \sigma}(t)] \rangle] \\
&= \sum_{\alpha_1 \alpha_2 \alpha_3} \left\{ V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) \langle \bar{A}_{\alpha_3 - \sigma}^+(t) \bar{A}_{\alpha_1 - \sigma}(t) \rangle F_{\alpha_2 \beta, \sigma}(t, t') \right. \\
&+ \sum_{\mu} \int_{t_0}^t d\tau [\Xi_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{r(U)}(t, \tau)] F_{\mu \beta, \sigma}(\tau, t') \\
&+ \left. \sum_{\mu} \int_{t_0}^{t'} d\tau [\Omega_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{(U)}(t, \tau)] G_{\mu \beta, \sigma}(\tau, t') \right\}. \tag{A1.4}
\end{aligned}$$

In equations (A1.1)–(A1.4) the G and F functions strictly appear within the TDHF approximation, although they have been replaced by those that we want to determine from the Dyson equations in integrodifferential form. Therefore equations (12)–(15) give an approximate solution to the time evolution of the desired G and F functions in a correlated system. At $t = t'$ we can obtain the average values of the different charge-state configurations from equations (A1.3) and (A1.4). By defining the correlation functions

$$\begin{aligned}
G_{\alpha \eta, \sigma}^{0(+)}(t, \tau) &= i \langle \bar{A}_{\alpha \sigma}^+(t) \bar{A}_{\eta \sigma}(t) \rangle \\
G_{\alpha \eta, \sigma}^{0(-)}(t, \tau) &= -i \langle \bar{A}_{\alpha \sigma}(t) \bar{A}_{\eta \sigma}^+(t) \rangle
\end{aligned}$$

the Ξ and Ω functions in equations (A1.1)–(A1.4) are given by

$$\begin{aligned}
\Xi_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{a(J)}(t, \tau) &= \frac{1}{2} (V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) - V_{\alpha_3 \xi \alpha_1 \alpha_2}(t)) \sum_{\lambda \eta \nu} (V_{\lambda \eta \nu \mu}(\tau) \\
&- V_{\eta \lambda \nu \mu}(\tau)) \Theta(\tau - t) [G_{\alpha_1 \eta, \sigma}^{0(+)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(+)}(t, \tau) G_{\nu \alpha_3, \sigma}^{0(-)}(t, \tau) \\
&- G_{\alpha_1 \eta, \sigma}^{0(-)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(-)}(t, \tau) G_{\nu \alpha_3, \sigma}^{0(+)}(t, \tau)] \\
\Xi_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{a(U)}(t, \tau) &= V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) \sum_{\lambda \eta \nu} V_{\lambda \eta \nu \mu}(\tau) [G_{\alpha_1 \eta, -\sigma}^{0(+)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(+)}(t, \tau) G_{\nu \alpha_3, -\sigma}^{0(-)}(t, \tau) \\
&- G_{\alpha_1 \eta, -\sigma}^{0(-)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(-)}(t, \tau) G_{\nu \alpha_3, -\sigma}^{0(+)}(t, \tau)] \Theta(\tau - t)
\end{aligned}$$

and

$$\begin{aligned}
\Omega_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{(J)}(t, \tau) &= \frac{1}{2} (V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) - V_{\alpha_3 \xi \alpha_1 \alpha_2}(t)) \sum_{\lambda \eta \nu} (V_{\lambda \eta \nu \mu}(\tau) \\
&- V_{\eta \lambda \nu \mu}(\tau)) [G_{\alpha_1 \eta, \sigma}^{0(+)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(+)}(t, \tau) G_{\nu \alpha_3, \sigma}^{0(-)}(t, \tau) \\
&+ G_{\alpha_1 \eta, \sigma}^{0(-)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(-)}(t, \tau) G_{\nu \alpha_3, \sigma}^{0(+)}(t, \tau)] \\
\Omega_{\xi \alpha_1 \alpha_2 \alpha_3 \mu, \sigma}^{(U)}(t, \tau) &= V_{\xi \alpha_3 \alpha_1 \alpha_2}(t) \sum_{\lambda \eta \nu} V_{\lambda \eta \nu \mu}(\tau) [G_{\alpha_1 \eta, -\sigma}^{0(+)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(+)}(t, \tau) G_{\nu \alpha_3, -\sigma}^{0(-)}(t, \tau) \\
&\times G_{\alpha_1 \eta, -\sigma}^{0(-)}(t, \tau) G_{\alpha_2 \lambda, \sigma}^{0(-)}(t, \tau) G_{\nu \alpha_3, -\sigma}^{0(+)}(t, \tau)].
\end{aligned}$$

The functions $\Xi_{\xi \mu, \sigma}(t, \tau)$ and $\Omega_{\xi \mu, \sigma}(t, \tau)$ in equations (12) and (13) in the text are defined as

$$\Xi_{\xi \mu, \sigma}(t, \tau) = \sum_{\alpha_1 \alpha_2 \alpha_3} \Xi_{\alpha_1 \alpha_2 \alpha_3 \mu, \sigma}(t, \tau)$$

and

$$\Omega_{\xi \mu, \sigma}(t, \tau) = \sum_{\alpha_1 \alpha_2 \alpha_3} \Omega_{\alpha_1 \alpha_2 \alpha_3 \mu, \sigma}(t, \tau)$$

where

$$\Xi^{r(J/U)}(t, \tau) = [\Xi^{a(J/U)}(\tau, t)]^*.$$

Appendix 2

In a time-dependent process described by the Anderson Hamiltonian, the explicit expressions for the $\tilde{\Xi}$ and $\tilde{\Omega}$ functions are given by

$$\tilde{\Xi}_\sigma^{r(V)}(t, \tau) = -i \Theta(t - \tau) \sum_k V_{ka}(t) V_{ka}(\tau) \exp\left(-i \int_\tau^t dx [\varepsilon_k - \varepsilon_a - U \langle \bar{n}_{a-\sigma}(x) \rangle]\right)$$

with

$$\tilde{\Xi}_\sigma^{a(V)}(t, \tau) = [\tilde{\Xi}_\sigma^{r(V)}(\tau, t)]^*$$

and

$$\begin{aligned} \tilde{\Xi}_\sigma^{r(U)}(t, \tau) &= -U^2 [g_{aa,-\sigma}^{0(+)}(t, \tau) g_{aa,\sigma}^{0(+)}(\tau, t) g_{aa,-\sigma}^{0(+)}(t, \tau) \\ &\quad - g_{aa,-\sigma}^{0(-)}(t, \tau) g_{aa,\sigma}^{0(-)}(t, \tau) g_{aa,-\sigma}^{0(-)}(\tau, t)] \Theta(t - \tau) \\ \tilde{\Xi}_\sigma^{a(U)}(t, \tau) &= U^2 [g_{aa,-\sigma}^{0(+)}(t, \tau) g_{aa,\sigma}^{0(+)}(t, \tau) g_{aa,-\sigma}^{0(+)}(\tau, t) \\ &\quad - g_{aa,-\sigma}^{0(-)}(t, \tau) g_{aa,\sigma}^{0(-)}(t, \tau) g_{aa,-\sigma}^{0(-)}(\tau, t)] \Theta(\tau - t) \\ \tilde{\Omega}_\sigma^{(U)}(t, \tau) &= U^2 [g_{aa,-\sigma}^{0(+)}(t, \tau) g_{aa,\sigma}^{0(+)}(t, \tau) g_{aa,-\sigma}^{0(+)}(\tau, t) + g_{aa,-\sigma}^{0(-)}(t, \tau) g_{aa,\sigma}^{0(-)}(t, \tau) g_{aa,-\sigma}^{0(-)}(\tau, t)] \end{aligned}$$

where $g_{aa,\sigma}^{0(+)}$ and $g_{aa,\sigma}^{0(-)}$ are defined as

$$\begin{aligned} g_{aa,\sigma}^{0(+)}(t, \tau) &= i \sum_{qocc} G_{aq,\sigma}^{0*}(\tau, t_0) G_{aq,\sigma}^0(t, t_0) \exp\left(-i \int_\tau^t dx [\varepsilon_a + U \langle \bar{n}_{a-\sigma}(x) \rangle]\right) \\ g_{aa,\sigma}^{0(-)}(t, \tau) &= -i \sum_{qempty} G_{aq,\sigma}^{0*}(\tau, t_0) G_{aq,\sigma}^0(t, t_0) \exp\left(-i \int_\tau^t dx [\varepsilon_a + U \langle \bar{n}_{a-\sigma}(x) \rangle]\right). \end{aligned}$$

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