PHYSICAL REVIEW A VOLUME 21, NUMBER 1 JANUARY 1980

K-shell-hole production, multiple-hole production, charge transfer, and antisymmetry

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(Received 26 January 1978; revised manuscript received 23 June 1978)

In calculating K-shell-hole production when an ion collides with an atom, account must be taken of the fact that processes involving electrons other than the K-shell electron can occur. For example, after making a K-shell hole an L-shell electron may be knocked into it, or an L-shell vacancy may be produced and the K-shell electron promoted to that vacancy in the "Fermi sea" of the target-atom orbitals. In 1973 a theorem was proved by one of the present authors demonstrating that all these multielectron processes cancel in an independent-particle model for the target atom. In this paper it is shown that the same thing occurs for hole production by charge transfer to the ion. The authors demonstrate that multihole production does *not* obey this simple rule and that the probability for multihole production is not the product of independent single-electron probabilities. The correct expressions that should be used for these processes are given, together with new results for charge-transfer processes accompanied by hole production.

I. INTRODUCTION

An intensive theoretical effort has been made recently to give some understanding of inner-shell ionization and charge-transfer processes when a fast projectile assumed moving on a classical predetermined path $\vec{R}(t)$ impinges on a target atom.[1] Reliable ionization and charge transfer calculations for such systems as protons on hydrogen have proven very difficult to produce. Analytic approximation schemes[1] give errors difficult to estimate and numerical schemes such as coupled state methods are very time consuming.[2] With such difficulties for the simple system of a proton on hydrogen it is unrealistic to think that progress can be made by immediately going to the full multielectron calculation. It is imperative, at least initially, to make some simplifying assumptions. The most promising of these is an independent particle model approximation, to wit assuming that the electrons have no interaction with each other but interact with the projectile and target nucleus with some average potential independent of electron configuration. To begin with, this treatment is clearly exact for bare ions impinging on hydrogenlike atoms. For many-electron systems it consists of assuming the electron-target interaction is some self-consistent Hartree-Fock potential. The advantage that inner-shell processes have in this regard is that the most important force is the electron nucleus attraction and screening effects are only of secondary importance. As a particular illustrative example consider a fully stripped oxygen ion impinging on a copper atom. To calculate K-shell hole production in this model we would assume that all the electrons move in the Hartree-Fock field of the atom in its ground-state configuration and in the pure Coluomb field of the ion. Of course we make no assertion that such a treatment is more than a first starting point for a full many-body calculation. If the oxygen ion captures seven electrons then the assumption that an eighth electron sees the full ionic potential is clearly grossly inaccurate. What is known is that such an event is extremely unlikely in the medium energy range of ionic collisions considered of interest here. However in this paper we are not concerned with justifying this independent particle model but rather with developing the correct expressions to use in calculating cross sections once this model is assumed.

Even with the assumption of independence one is still faced with the requirement that the system wave function be antisymmetric in the electron indices. This correlation cannot necessarily be ignored. If one is working in first-order perturbation theory K-shell-hole production is correctly obtained by calculating the process for the K electron to be lifted above the "Fermi sea" of occupied target orbitals, i.e., the other electrons play a passive role. This is because to excite an L-shell electron *and* a K-shell electron involves two projectile-electron interactions, which is beyond first order. If one wishes to obtain a more accurate expression for K-shell hole production one can calculate the amplitude for an isolated K-shell electron to be lifted above the Fermi sea to higher order, ignoring the presence of other electrons completely. This is what is done in the treatment by Basbas *et al.*[1] with the idea of "increased binding." However a little reflection will show that this approach is not necessarily consistent because if we go beyond first order, multielectron processes are now of equal importance. We might first create an L-shell hole and then a K-shell hole not by lifting the K electron above the Fermi sea but rather by filling the L-shell vacancy. This will add to the K-shell hole production cross section. Alternatively, having created a K-shell hole it could be refilled from the L shell. This would subtract from the process. The complication of such a calculational approach will be evident to the reader. What is needed is a simplifying idea. This is provided if we first note that for K-shell hole production we are concerned with only the final state of the target K shell. Vacancies in the other orbitals are irrelevant. Because of this it is possible to use closure and prove a theorem, viz., K-shell hole production is correctly calculated by ignoring completely the presence of all the other electrons. The cross section is identical to that one would obtain by considering the projectile incident on a single electron system and calculating all processes, in which the electron is removed from the K shell to any orbital not initially occupied in the original many electron system.

This theorem was proven in 1973.[3] It has been discussed by McGuire *et al.*[4] It is the basis on which higher-order calculations of x-ray production rest. The proof given though was deficient in that charge transfer from the K shell to the projectile was not included as a possible channel. And further the projectile was considered to be initially a bare ion with no attached electrons. In this paper (Sec. III) we rectify that situation. We find that we simply have to add to the isolated single electron excitation and ionization cross sections already calculated the contribution from charge transfer to states not occupied initially on the projectile. Indeed this is once again exactly what has been assumed without proof by other authors.[5]

The fact that for K-shell hole production the process proceeds independently of the other electrons might lead the unwary investigator to assume that a similar result is true for all similar processes. This certainly is not the case for such simple generalizations as multihole production or charge transfer accompanied by hole production in a specified state. In particular, if we introduce the notation that ρ_j is the probability for producing a hole in the orbital state labeled by j, initially occupied in the target, our first theorem states that

$$\rho_j = 1 - \sum_k |a_{kj}|^2 .$$

Here a_{kj} is the amplitude for a transition from state j to k and k is taken over all orbitals initially occupied. It is natural in view of our proceeding discussion to guess that the probability for producing two holes in states 1 and 2, ρ_{12}, would be given by $\rho_{12} = \rho_1 \rho_2$.

And indeed this is what has been assumed.[6] However, the correct result is a determinant

$$\rho_{12} = \begin{vmatrix} 1 - \sum_k |a_{1k}|^2 & -\sum_k a_{1k} a_{2k}^* \\ -\sum_k a_{2k} a_{1k}^* & 1 - \sum_k |a_{2k}|^2 \end{vmatrix} \leq \rho_{12} .$$

This is demonstrated in Sec. IV. The result for producing n holes $\rho_{12\cdots n}$ is the determinant of the n by n matrix the ijth element of which is $(\delta_{ik} - \sum_k a_{ik} a_{jk}^*)$.

Further, it is demonstrated that antisymmetry also plays an important role in charge transfer accompanied by hole production. The expression used to analyze the experiment of Cocke *et al.*[7] is incorrect. This is done in Sec. V.

The importance of all these results is that it has been shown that for ion-atom collisions all the single electron amplitudes a_{ij} can indeed be calculated very rapidly and accurately whenever there is asymmetry between the projectile charge and the target nuclear charge.[8] The methods have been developed for ionization and this work is essential to an understanding of charge transfer effects, which have been demonstrated to play a part in x-ray production.[5]

To prove the results that we wish it is necessary to establish a theorem for the time dependent perturbation of a single electron system in the semiclassical limit. As noted by Shakeshaft and Spruch[9] there is an annoying difficulty with long-range forces for non-neutral systems that are of interest here. As a preliminary to the main results in this paper we next examine this difficulty and produce a prescription for avoiding it. We do not claim this is the best solution to the problem, only a correct one.

II. ORTHOGONALITY AND COMPLETENESS

In the independent particle model for the electrons the total wave function for the system, $\psi^{(-)}$, is factored into an antisymmetrized product of single-particle channel wave functions $\psi_\alpha^{(-)}(\xi_i, t)$. Here ξ_i denotes position $\vec{r}_i$ and spin of the ith electron. The label α denotes the quantum numbers of the orbital $\chi_\alpha^{(-)}(\xi_i, t)$ to which $\psi_\alpha^{(-)}(\xi_i, t)$ develops as $t \to \infty$, i.e., when the projectile and target are far apart. The states $\chi_\alpha^{(-)}(\xi_i, t)$ are usually thought of as falling into three classes: the electron bound on the projectile, or on the target, or in some scattering state with specified asymptotic energy and momentum. The superscript, redundant in the first two cases, implies incoming spherical wave boundary conditions. For Coulomb forces as we shall see these states warrant further discussion which will be given below. In calculating the cross section formulas in the following sections we will need to evaluate sums over a complete set of $\psi_\alpha^{(-)}$. Hence an important question to be dealt with is what comprises a complete orthogonal set of system orbitals $\psi_\alpha^{(-)}$ at time t. We first discuss the completeness and orthogonality of the $\chi_\alpha^{(-)}(\xi_i, t)$. Having established this, the completeness and orthogonality of the $\psi_\alpha^{(-)}(\xi_i, t)$ then follow from the unitarity of the time-development operator. That is, $(\psi_\alpha^{(-)}, \psi_\beta^{(-)})$ is a constant (independent of time) and so therefore equals $(\chi_\alpha^{(-)}, \chi_\beta^{(-)})$.

The only solutions of the time dependent Schrödinger equation which have been shown to be orthogonal and complete are stationary states. Kato[10] has shown the important property that the Schrödinger operator is self-adjoint, and Ikebe[11] has proven that the bound states and scattering states of a fixed time independent potential are orthogonal and complete. Dollard[12] extended these considerations to scattering with Coulomb forces. It is however easy to show that with Coulomb forces all the states $\chi_\alpha^{(-)}(\xi_i, t)$ cannot be stationary or therefore well defined by the label α. The problem lies firstly with the infinite in number, barely bound Rydberg states. Consider the system under discussion to be a bare ion charge Z_N incident on a hydrogen atom, and let us consider the electron to be left on the proton in some high Rydberg state. For the ion at some large finite distance R from the proton, there will be an infinite number of Rydberg states, principal quantum number n greater than n_c, which have a binding energy less than the perturbing attractive ionic potential. Here n_c is defined by

$$e^2/(2a_0 n_c^2) = Z_n e^2/R .$$

An electron placed in such a state will have no difficulty in tunneling away from the proton and eventually ending up on the ion. And even as R is increased arbitrarily large the long-range nature of the Coulomb force assures an infinite number of levels arbitrarily close to the continuum of the proton-electron system that will not be in well-defined bound states, and therefore not in stationary states as the ion moves. A similar statement may be made about the low-energy scattering states of such a system.

Of course these Rydberg states will rarely be of any importance in any physical process. They are merely a mathematical inconvenience, but one that must be dealt with nevertheless if we are to proceed in an orderly fashion. A simple way out of this difficulty is to adiabatically stop the ion at some large but finite time t_L. Because we wish to preserve time reversal symmetry we also assume the ion is slowly accelerated from rest initially before the collision at some time $-t_L$. The electron is now moving, for times greater than t_L, in a fixed static potential, $V(t_L)$, provided by the proton and ion, both at rest a large but *finite* distance away from each other. The electronic bound states and scattering states of such a system are now clearly defined and give the set $\chi_\alpha^{(-)}(\xi_i, t)$. That is they are eigensolutions of the Schrödinger equation

$$\left(\frac{-\hbar^2}{2m_e}\nabla_r^2 + V(t_L)\right)\chi_\alpha^{(-)}(\xi_i, t) = i\hbar\frac{\partial}{\partial t}\chi_\alpha^{(-)}(\xi_i, t) ,$$

with definite energy E_α, satisfying the boundary condition specified above. The time dependence of these states is simply $\exp(-iE_\alpha t/\hbar)$. Ikebe[11] has shown such a system of states to be complete and orthogonal. The "deeply" lying bound states can be made arbitrarily close in all characteristics to the isolated proton-electron and ion-electron bound states that are usually regarded as the "final states" of a scattering process. Further, as long as the ion is slowed down adiabatically "shake off" processes may be made arbitrarily small. Of course the barely bound states of the isolated system will depend on t_L and the slowing process but if these are not of physical interest then that is of no concern. We should also add that in reality the projectile is often accelerated or deflected before the electronic state is measured.

Having established that $\chi_\alpha^{(-)}(\xi_i, t)$ are complete and orthogonal the uniqueness and unitarity[12] of the time development operator U assures that $\psi_\alpha^{(-)}(\xi_i, t)$ will be well defined, orthogonal and complete, e.g.,

$$(\psi_\alpha^{(-)}(t), \psi_\beta^{(-)}(t)) = (\chi_\alpha^{(-)}(t_L), U^\dagger(t, t_L)U(t, t_L)\chi_\beta^{(-)}(t_L))$$
$$= \delta(\alpha, \beta) .$$

An alternative approach to the problem is to replace all Coulomb forces in the system by some cutoff potential. If the reader prefers this approach the proof of orthogonality proceeds smoothly. There is now no problem with high Rydberg states as there are none. The only tricky thing is to prove that the scattering states are orthogonal to the bound states. First we must demonstrate that the scattering states are stationary. We define a state to be stationary if it has definite energy. Thus the hydrogen atom moving with relative velocity v with respect to a fixed frame is considered stationary even though it has a time dependence other than $\exp(-iE_\alpha t/\hbar)$. The stationary nature of the scattering states may be established by using the multiple scattering expansion for two potentials asymptotically far apart.[13] The orthogonality can then be established by showing that in the region of the target $\chi_\alpha^{(-)}$ behaves like a target scattering state and in the region of the projectile it behaves like a projectile scattering state. We do not give more details here as we find the cutoff method lacking in aesthetic appeal.

Finally we remark that in the coupled-state approach to the problem the fact that the channel wave functions are orthogonal and complete has been used since the development by Wilets and Gallaher[2] of the "unitarity check" which is merely an assertion of the same result in a different language.

Having given our reasoning as to why the $\psi_\alpha^{(-)}(\xi_i, t)$ are orthogonal and complete we now apply this result to the much more interesting physics problem at hand.

III. K-SHELL-HOLE PRODUCTION

As stated in Sec. I, we wish to determine the correct expressions for the probabilities of various inner-shell-hole production and charge-transfer events, in the independent particle model but allowing for antisymmetry. In the independent particle model the initial ($t< -t_L$) state of the target is described by a determinantal wave function $\phi(\xi_1, \ldots \xi_N, t)(N!)^{-1/2}$. This is the determinant of a $N\times N$ matrix the ijth element of which is $\chi_i^T(\xi_j, t)$. Here $\chi_i^T(\xi_j, t)$ is the ith single particle bound-state wave function of the target, and ξ_j as stated in Sec. II gives the space and spin coordinates of the jth electron. There are N electrons initially bound to the target nucleus. Note that in the independent particle model a state of the system is specified by stating which orbitals are occupied. For the target initial state we are considering the orbitals $\chi_1^T \ldots \chi_N^T$ are occupied.

For a bare (structureless) projectile incident on a target in the above independent particle model initial state, the scattering amplitude for producing a final state $\alpha \cdots \eta$ is given by

$$A_{\alpha\cdots\eta} = (\psi_\alpha^{(-)}(\xi_1, t) \cdots \psi_\eta^{(-)}(\xi_N, t) \times \phi(\xi_1, \ldots \xi_N, t))(N!)^{-1/2}. \quad (1)$$

Here, and in the following, the time t is to be taken such that $t< -t_L$. (As defined in Sec. II, $-t_L$ is the time in the adiabatic approximation approach at which the target and projectile are slowly accelerated from rest.) The final state $\alpha \cdots \eta$ is specified by stating the single particle wave functions (either target bound orbitals, projectile bound orbitals, or continuum orbitals) that are to be occupied at $t> t_L$. We have used the idempotent property of the antisymmetrizer to write the expression for the amplitude so that a simple orbital product, not a determinant, appears on the left in the inner product.

We first calculate the probability ρ_1 of producing a final state in which there is a K-shell hole (in a particular spin orbital χ_1^T) in the target, but where the final state of the system is otherwise unrestricted. We denote by χ_1^T the target K-shell spin orbital which we require to be occupied initially and to be unoccupied in the final state of the system. Then ρ_1 is given by squaring $A_{\alpha\cdots\eta}$ and summing over all final-state orbital occupations $\alpha \cdots \eta$, except the restriction is imposed that the orbital χ_1^T in which the K-shell hole is to be created must *not* be occupied in any of the $\alpha \cdots \eta$ included in the sum. With the notation that

$$P_{1j} = \psi_1^{(-)}(\xi_j', t)\psi_1^{(-)}(\xi_j, t)$$

we obtain, on using the closure property established in the previous section to evaluate the sum over final-state orbital occupations,

$$\rho_1 = \int \prod_{i=1}^N d\xi_i \prod_{i=1}^N d\xi_i' \phi^*(\xi_1', \ldots \xi_N', t) \times \prod_{j=1}^N (\delta(\xi_j', \xi_j) - P_{1j})\phi(\xi_1, \ldots \xi_N, t)(N!)^{-1}. \quad (2)$$

We have used primed and unprimed ξ_i's to denote the two separate integrations over coordinates in the $A^*_{\alpha\cdots\eta}$ and $A_{\alpha\cdots\eta}$ factors appearing in $\rho_1 = |A_{\alpha\cdots\eta}|^2$.

Since $P_{1j}P_{1i}\phi(\xi_1, \ldots \xi_N, t)$ produces a function which is symmetric in the indices ξ_j', ξ_i', whereas $\phi(\xi_1', \cdots \xi_N', t)$ is antisymmetric in these indices, matrix elements of the form $(\phi, P_{1j}P_{1i}\phi)$ are zero. To see this in more detail, use the idempotent property of the antisymmetrizer to replace the antisymmetrized (determinantal) function on the right in Eq. (2) by a simple orbital product

$$\rho_1 = \int \prod_{i=1}^N d\xi_i \prod_{i=1}^N d\xi_i' \phi^*(\xi_1', \ldots \xi_N', t) \times \prod_{j=1}^N [\delta(\xi_j', \xi_j) \ldots P_{1j}]\chi_1^T(\xi_1, t) \cdots \chi_N^T(\xi_N, t). \quad (3)$$

Terms of the form $(\phi, P_{1j}P_{1i}\phi)$ thus become

$$(\phi, P_{1j}P_{1i}\phi) = (\psi_1^{(-)}, \chi_j^T)(\psi_1^{(-)}, \chi_i^T) \times (\phi_1(\xi_1' \cdots \xi_N', t), \chi_1^T(\xi_1', t) \cdots \psi_1^{(-)}(\xi_i', t) \cdots \psi_1^{(-)}(\xi_j', t) \cdots \chi_N^T(\xi_N', t)). \quad (4)$$

In the last factor ϕ is antisymmetric in ξ_i', ξ_j', whereas the function in the right is symmetric in these indices. Hence the integral is zero.

With the above observation, Eq. (2) for ρ_1 reduces to

$$\rho_1 = \int \prod_{i=1}^{N} d\xi_i \prod_{i=1}^{N} d\xi_i' \phi^*(\xi_1', \cdots \xi_N', t) \times \left(\prod_{j=1}^{N} \delta(\xi_j', \xi_j) - \sum_{k=1}^{N} P_{1k} \prod_{j\neq k}^{N} \delta(\xi_j', \xi_j) \right) \prod_{i=1}^{N} \chi_i^T(\xi_i, t) . \quad (5)$$

Using the orthogonality of the $\chi_i^T(\xi_i, t)$, this then can be written

$$\rho_1 = 1 - \sum_{k=1}^{N} |a_{1k}|^2 , \quad (6)$$

where a_{1k} is the one-electron matrix element, $a_{1k} = (\psi_1^{(-)}, \chi_k^T)$, and the sum on k is over all orbitals initially occupied in the target. We note that $|a_{1k}|^2$ is the probability of the electron initially in orbital k being scattered into orbital 1, the orbital where the K-shell hole is to be produced. Thus we may interpret ρ_1 as the probability of *not* scattering *any* electron into the orbital χ_1^T, including the electron originally in this orbital. Alternatively, using time reversal, i.e., $|a_{1j}|^2 = |a_{j1}|^2$, we may interpret ρ_1 as the probability of not scattering the K-shell electron into an initially occupied orbital. Using the completeness of the target bound orbitals, projectile bound orbitals, and the continuum orbitals, we can also write

$$\rho_1 = \sum_{k>N} |a_{k1}|^2 , \quad (7)$$

where the symbol k runs over the unoccupied bound orbitals of the target, the bound orbitals of the projectile, and the continuum orbitals. This expression says that the probability of producing a hole in the initially occupied orbital χ_1^T is just given by the sum of the probabilities of exciting an electron from this orbital to any of the initially unoccupied orbitals of the projectile-target system. This is exactly the cross section one would calculate if only a single target electron were interacting with the projectile. This result is the generalization to include charge transfer of the one previously obtained.[3] Calculations in the independent particle model[8] have been based on it though the derivation has not been presented before. Note that the expected value of the number of K-shell vacancies, as opposed to the probability for a hole in a specific K-shell spin orbital (labeled 1 or 2 for the two spin states), is given by $\rho_1 + \rho_2 = 2\rho_1$ for spin independent forces.

This becomes clear if we consider the following. The probability ρ_1 is of course *inclusive* of producing two holes in the K shell. Thus with the notation described above the probability for producing one hole *only* in the K shell (state 1) is $\rho_1 - \rho_{12}$. Similarly the probability for producing the other hole only (state 2) is $\rho_2 - \rho_{12}$. The probability for producing two holes is of course ρ_{12}. This latter process leads to *two* holes (and therefore possibly *two* x-rays); the former two processes lead to one hole. Hence as stated above, the expected value for the number of K-shell vacancies is $\rho_1 - \rho_{12} + \rho_2 - \rho_{12} + 2\rho_{12} = \rho_1 + \rho_2 = 2\rho_1$.

Of course everything we have proven for K-shell hole production applies equally well to any other state. It would be difficult, however, to justify the independent particle model for the outer electrons and there would be important correlations other than antisymmetry.

Lastly we remark that there is no meaningful distinction in our formulism between target states and projectile states. Thus systems in which several electrons are initially present on the projectile give the same result as Eq. (6) but now we should consider the sum over k to run over all the states initially occupied both on the target and projectile.

IV. MULTIPLE-HOLE PRODUCTION

In Sec. III we demonstrated that other electrons may be ignored for single-hole production. Here we demonstrate that this independence is true for two-hole production if the spins of the electron holes are different; it is not true when they are the same, e.g., when we have in mind creating simultaneously a K-shell and L-shell hole with the same spin.

To calculate the probability of producing a hole in spin orbital χ_1^T and also in χ_2^T, we, as in Sec. III, square $A_{\alpha\cdots\eta}$ and sum over all final orbital occupations that correspond to holes in χ_1^T and χ_2^T. That is, we exclude from the sum those orbital configurations that have either (or both) of χ_1^T or χ_2^T occupied. The closure property of our complete orthogonal set of single electron orbitals can again be used to evaluate the sum. Defining the operator P_{2j} analogous to the operator P_{1j} in the previous section we obtain the probability ρ_{12} for producing holes in each of spin orbitals 1 and 2 as

$$\rho_{12} = \int \prod_{i=1}^{N} d\xi_i \prod_{i=1}^{N} d\xi_i' \phi^*(\xi_1', \cdots \xi_N', t) \times \prod_{j=1}^{N} (\delta(\xi_j, \xi_j') - P_{1j} - P_{2j}) \prod_{i=1}^{N} \chi_i^T(\xi_i, t) . \quad (8)$$

This may be simplified by the same methods used previously to

$$\rho_{12} = 1 - \sum_{i=1}^{N} (|a_{1i}|^2 + |a_{2i}|^2) + \int \prod_{i=i}^{N} d\xi_i \prod_{i=1}^{N} d\xi_i' \phi^*(\xi_1', \ldots \xi_N', t) \times \sum_{k<j}^{N} (P_{1j}P_{2k} + P_{2j}P_{1k}) \times \prod_{m\neq k,j}^{N} \delta(\xi_m', \xi_m) \prod_{i=1}^{N} \chi_i^T(\xi_i, t) . \quad (9)$$

Here we use the notation $a_{2i} = (\psi_2^{(-)}, \chi_i^T)$, in analogy to the previous definition for a_{1i}. The last term in Eq. (9) is of a type not previously encountered. Writing it as B we note

$$B = \sum_{i<j} (\chi_j(\xi_j')\chi_i(\xi_i') - \chi_i(\xi_j')\chi_j(\xi_i'), \psi_1^{(-)}(\xi_j')\psi_2^{(-)}(\xi_i')a_{1j}a_{2i} + \psi_2^{(-)}(\xi_j')\psi_1^{(-)}(\xi_i')a_{2j}a_{1i})$$
$$= \sum_{i<j} (|a_{1j}|^2|a_{2i}|^2 - a_{1i}^* a_{2j}^* a_{1j} a_{2i} + |a_{2j}|^2|a_{1i}|^2 - a_{2i}^* a_{2j} a_{1i} a_{1j}^*).$$

To simplify the notation in the following steps we let $F(i,j)$ represent the expression being summed. Thus

$$B = \sum_{i=1}^{N} \sum_{j=i+1}^{N} F(i,j) = \sum_{i=1}^{N} \sum_{j=i}^{i} F(i,j). \tag{10}$$

The latter step follows as $F(i,i)$ is zero. Proceeding, we write

$$B = \frac{1}{2}\left(\sum_{i=1}^{N}\sum_{j=1}^{N} F(i,j) + \sum_{j=1}^{N}\sum_{i=1}^{j} F(i,j)\right)$$
$$= \frac{1}{2}\left(\sum_{i=1}^{N}\sum_{j=i}^{N} F(i,j) + \sum_{i=1}^{N}\sum_{j=1}^{i} F(j,i)\right)$$
$$= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} F(i,j). \tag{11}$$

The latter step follows from noting $F(i,j) = F(j,i)$. Thus we demonstrate that

$$\rho_{12} = \left(1 - \sum_{k=1}^{N} |a_{1k}|^2\right)\left(1 - \sum_{k=1}^{N} |a_{2k}|^2\right) - \left|\sum_{k=1}^{N} a_{1k} a_{2k}^*\right|^2. \tag{12}$$

All sums are over the orbitals initially occupied. The first term in this expression may be identified as $\rho_1\rho_2$ where ρ_{12} is the probability of forming a hole in orbital 1 and ρ_2 is the probability of forming a hole in orbital 2. The last term subtracts from this and may be thought of as the probability of knocking particle 2 into the hole 1, or vice versa, through an intermediate state k. *Thus the correlation produced by antisymmetry destroys the independence of probability for this process.*

It is interesting to note for spin independent Coulomb excitation that if the orbitals 1 and 2 are of *opposite* spin (for example the two K-shell orbitals), then when a_{1i} is nonzero a_{2i} must be zero. Thus in this case we recover

$$\rho_{12} = \rho_1\rho_2, \tag{13}$$

the probability of simultaneously producing both holes is just the product of probabilities for independently producing each hole.

Even for holes in orbitals of the same spin the result of Eq. (13) is obtained if the antisymmetry requirement is not imposed on the wave functions, i.e., if the electrons are treated as distinguishable particles. Equation (12) thus shows that the correlation produced by antisymmetry has yielded a probability ρ_{12} which is always *less* than the simple product of independent probabilities one obtains if antisymmetry is not imposed. The precise amount by which ρ_{12} differs from $\rho_1\rho_2$ will be answered in numerical calculations now being performed by the present authors.

The generalization of the result of Eq. (12) to the case of many-hole production can be inferred by viewing ρ_{12} as the determinant of the matrix M,

$$M = \begin{pmatrix} 1 - \sum_{k=1}^{N} |a_{1k}|^2 & -\sum_{k=1}^{N} a_{1k}a_{2k}^* \\ -\sum_{k=1}^{N} a_{2k}a_{1k}^* & 1 - \sum_{k=1}^{N} |a_{2k}|^2 \end{pmatrix}. \tag{14}$$

Thus the probability of producing n holes, $\rho_{1\cdots n}$, is given by the determinant of the $n\times n$ matrix whose matrix elements are $M_{ij} = \delta_{ij} - \sum_k a_{ik}a_{jk}^*$. This gives, for example, that the probability for producing three holes is

$$\rho_{123} = \rho_1\rho_2\rho_3 - \left|\sum_{i=1}^{N} a_{1i}a_{2i}^*\right|^2 \rho_3 - \left|\sum_{i=1}^{N} a_{1i}a_{3i}^*\right|^2 \rho_2 - \left|\sum_{i=1}^{N} a_{2i}a_{3i}^*\right|^2 \rho_1 - 2\,\mathrm{Re} \times \left(\sum_{i=1}^{N} a_{1i}a_{2i}^* \sum_{j=1}^{N} a_{2j}a_{3j}^* \sum_{k=1}^{N} a_{3k}a_{1k}^*\right). \tag{15}$$

All sums are again over the initially occupied states of the target projectile system. That this expression is indeed correct has been explicity verified. For many-hole production it is the off-diagonal elements in M that prevent $\rho_{1\cdots n}$ from being given by the product of independent probabilities $\rho_1 \cdots \rho_n$. As far as we know, the result of Eq. (12) for two-hole production, and its generalization to many-hole production described above, has not been previously presented; it is a new result.

Our result, that for producing holes in orbitals of the same spin the probability is not simply a product of single-hole production probabilities, of course alters the simple binomial form discussed by several authors[4] for multiple hole production.[4,6] This binomial distribution arises from writing

$$1 = (1 - \rho + \rho)^N = \sum_{m=0}^{N} b_m \rho^m (1-\rho)^{N-m}. \tag{16}$$

Here ρ is the probability for producing a single hole, in any initially occupied orbital of the target. Thus the term $\rho^m(1-\rho)^{N-m}$ is meant to refer to the probability of producing m holes (only m holes; no more, no fewer). But our results show that the probability of producing m holes is not simply the m-fold product of single-hole production probabilities.

We emphasize that our ρ_1 is the probability of producing a hole in orbital 1, irrespective of the final orbitals of each of the electrons. That is, in ρ_1 are included all processes in which the hole in orbital 1 is accompanied by none, one, or many additional holes, and a similar statement can be made about our multiple hole production probabilities. But our formalism also yields expressions for probabilities such as ρ_1^2, the probability for producing a hole in orbital 1 while at the same time *not* producing a hole in orbital 2. We can write, for example, $\rho_1 = \rho_{12} + \rho_1^2$, which in turn says that

$$\rho_1^2 = \sum_{i=1}^{N} |a_{2i}|^2 \left(1 - \sum_{k=1}^{N} |a_{1k}|^2\right) + \left| \sum_{i=1}^{N} a_{1i} a_{2i}^* \right|^2 . \quad (17)$$

Thus for ρ_1^2, as for ρ_{12}, there is an extra term which prevents it from being written as a product of the independent probabilities for producing a K-shell hole and for scattering (perhaps elastically) an electron into orbital 2.

V. CAPTURE IN THE PRESENCE OF A HOLE

An interesting process is that in which a K-shell hole in the target is formed, accompanied by capture to a definite orbital χ_J^P of the projectile. Here then we are interested in the amplitude $A_{\alpha\cdots\eta}$ [Eq. (1)], where each of α through η can take on all values *except* the hole state χ_1^T, and one of α through η *must* refer to χ_J^P.

Let us first of all though consider just capture to the orbital χ_J^P, with no regard to the hole states also being produced. This probability ρ^J is given by summing $|A_{\alpha\cdots\eta}|^2$ over all final orbital occupations, but requiring that χ_J^P be always occupied. This yields

$$\rho^J = \int \prod_{i=1}^{N} d\xi_i \prod_{i=1}^{N} d\xi_i' \phi^*(\xi_1', \cdots \xi_N', t) \times \sum_{j=1}^{N} P_{Jj} \prod_{k\neq j}^{N} \delta(\xi_k, \xi_k') \prod_{i=1}^{N} \chi_i^T(\xi_i)$$
$$= \sum_{j=1}^{N} |a_{Jj}|^2 = 1 - \rho_J . \quad (18)$$

That is, we simply add the probabilities for capture from all orbitals initially occupied. This result could have been deduced directly from Eq. (6) by merely replacing the state 1 by state J throughout the proof.

The probability ρ_1^J of capture to the orbital χ_J^P while leaving a hole in χ_1^T is given by summing $|A_{\alpha\cdots\eta}|^2$ over all final orbital occupations that leave a hole in χ_1^T and χ_J^P occupied. This yields

$$\rho_1^J = \sum_{i=1}^{N} |a_{Ji}|^2 - \sum_{i\neq j}^{N} (\chi_i(\xi_i)\chi_j(\xi_j) - \chi_i(\xi_j)\chi_j(\xi_i), \psi_J^{(-)}(\xi_i) a_{Ji} \psi_1^{(-)}(\xi_j) a_{1J})$$
$$= \sum_{i=1}^{N} |a_{Ji}|^2 - \sum_{i,j=1}^{N} (|a_{Ji}|^2 |a_{1j}|^2 - a_{Jj}^* a_{Ji} a_{1i}^* a_{1j}) . \quad (19)$$

The last step follows as the term involving $i=j$ is zero. Proceeding,

$$\rho_1^J = \sum_{i=1}^{N} |a_{Ji}|^2 \left(1 - \sum_{j=1}^{N} |a_{1j}|^2\right) + \left| \sum_{j=1}^{N} a_{1j} a_{Jj}^* \right|^2 . \quad (20)$$

Here as before, if χ_J^P and χ_1^T are orbitals of different spin we obtain a sensible uncorrelated result, the first term in Eq. (20). The probability for capture accompanied by two (or more) holes may be deduced in a similar way.

Once again we could have deduced this result by noting that it is nothing more than $\rho_1 - \rho_{1J}$, because if there is not a hole in state J there must be a particle in it. Compare Eq. (20) for example to Eq. (17).

As for our multiple-hole production cross sections, we believe the result of Eq. (20) to be new. Note that if one takes only the $|a_{J1}^* a_{11}|^2$ term in the last sum, and approximates $1 - \sum_{j\neq 1}^{N} |a_{1j}|^2$ by unity when multiplying $|a_{J1}|^2$, one will get the equation

$$\rho_1^J \approx |a_{J1}|^2 + \sum_{i\neq 1}^{N} |a_{Ji}|^2 \left(1 - \sum_{k=1}^{N} |a_{1k}|^2\right) . \quad (21)$$

In this approximate expression ρ_1^J is given by the probability of the K-shell electron itself being captured, plus the probability of capture from any other state, for example the L shell, accompanied by production of a hole in the K shell by any process, for example ionization. In a recent set of experiments Cocke *et al.*[7] observed the production of a K-shell hole accompanied by charge transfer, for protons incident on Ar, Ne, O_2, and N_2. They interpreted their results (apparently on physical grounds) in the above approximation. They further argued that the second term of Eq. (21) is somewhat smaller than the first, and that their results, approximately corrected for such effects, could thus be interpreted in terms of capture from the K shell. It will be of great interest to test the validity of this argument, and further to test the validity of the approximate Eq. (21) itself, by an accurate evaluation of Eq. (20). Such numerical calculations are being carried out by the present authors. Note that there will be corrections to the approximate Eq. (21) of the form $a_{j1}^* a_{11} a_{Jj} a_{1J}^*$, for $j \neq 1$. These interference type terms contain the elastic amplitude a_{11} and thus may reasonably be expected to be appreciable, compared to the terms in Eq. (21).

VI. CONCLUSION AND DISCUSSION

We have extended the validity of the proof that spectator electrons on the target may be ignored in single hole production in the independent particle model to include charge transfer to the projectile as a possible mechanism. The probability is that obtained by calculating all processes in which the active electron is promoted to any state not initially occupied on the target or projectile. We have avoided the formal difficulties with the long range nature of Coulomb forces by proposing an adiabatic slowing to rest of the projectile and target systems. We assert as physically reasonable that this will not materially affect most transitions of interest to the experimentalist. It may therefore be left out of an actual calculation if desired, i.e., the standard matrix elements[5] including translation factors may be used in evaluating charge transfer to all but the most loosely bound Rydberg states.

We have also demonstrated that the spectator electrons do play a role in more complicated processes such as two-hole production and this effect must be taken into account.

The actual importance of these results to real processes is yet to be determined. Amplitudes are needed for transitions between all initially occupied states of the system. These are fortunately available with the U-matrix approach[8] already developed and we hope to present some comparisons with experiment shortly.

ACKNOWLEDGMENT

This work was supported by the Center for Energy and Mineral Resources, Texas A & M University.

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