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LETTER TO THE EDITOR

On the role of shake-off in single-photon double ionization

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Abstract
The role of shake-off for double ionization of atoms by a single photon with finite energy has become the subject of debate. In this letter, we attempt to clarify the meaning of shake-off at low photon energies by comparing different formulations appearing in the literature and by suggesting a working definition. Moreover, we elaborate on the foundation and justification of a mixed quantum-classical ansatz for the calculation of single-photon double ionization.

It is well known that the double-to-single cross section ratio for ionization of atoms by a single photon does not vanish at high photon energies. Rather, it approaches a finite constant which can be explained in the framework of a sudden approximation by the so-called shake-off mechanism. While shake-off is well defined in the asymptotic high-energy limit, its meaning at finite energies is less clear and has been the subject of debate recently. In fact, a number of definitions can be found in the literature, e.g., [1–7]. Some of these definitions are based on formal diagrammatic perturbation expansion techniques [3, 5], others on more general physical arguments [2, 4] and others on a simple extension of the sudden approximation idea to finite energies [1, 6, 7]. Most of them (with the exception of [3], see below) have in common that they approach the well known asymptotic expression at high energies. At low and intermediate energies, however, they may differ markedly (e.g., some show a monotonic dependence on energy while others have a maximum at some finite energy, some even exceed the total double-to-single cross section ratio measured experimentally). Thus, to date no unique definition for shake-off at finite energies exists, and it is not obvious what 'the best' definition might be. On the other hand, in particular in connection with the interpretation of experimental data, attention has been given to the question of which physical mechanisms dominate double ionization and at which energies the different mechanisms are important [8].

One may argue that a satisfying definition of shake-off would be one based on physical principles in addition to mathematical rigor. Hence, a 'good' definition should separate shake-off as much as possible from other ionization mechanisms. Clearly, such a separation is not strictly possible in the presence of other available routes to ionization and can only be approximate, which makes the discussion of a shake-off *mechanism* a somewhat delicate issue. In comparing calculations with experiments, for example, one should always keep in mind that no strict one-to-one correspondence between a shake-off mechanism as an approximate physical picture and a separate calculation of shake-off can be expected due to the neglect of interference between possible decay routes. Nevertheless, since such simple physical pictures, to the extent of their applicability, can be very valuable for our intuitive understanding of physical processes; a definition separating shake-off from 'non-shake-off' would seem most rewarding conceptually. One such definition has recently been given by Schneider, Chocian and Rost [7] (hereafter referred to as SCR), where the single-photon double ionization process has been described in terms of two separate contributions, namely 'shake-off' and 'knock-out'. The method used in SCR was shown to lead to excellent agreement with experimental and *ab initio* calculations for double ionization from the ground state [7, 9], and very recently also from excited states [10], of helium. Thus, it suggests itself as a more or less natural 'operational' definition of shake-off in the framework of the 'half-collision' picture of single-photon multiple ionization [4, 11].

The calculation reported in SCR starts from a mixed quantum-classical ansatz that is based on the separation of the photoabsorption process (which is not treated explicitly in the calculation) from the subsequent evolution of the system. It treats this evolution (i.e. the redistribution of the energy between the two electrons) in the spirit of an (e, 2e)-like process with the additional possibility of shake-off. Such a 'half-collision' picture has been originally suggested by Samson [11] and elaborated by Pattard and Burgdörfer [4], allowing for shake-off processes which are not taken into account in Samson's original model. In the SCR ansatz, the (e, 2e)-like ('knock-out') part of the cross section is calculated using a classical trajectory Monte Carlo method, to which the shake-off as a purely quantum mechanical process is added on top. In this spirit, shake-off is introduced as a more or less *ad hoc* quantum correction to an essentially classical treatment. Here, we start from a fully quantum mechanical expression and see which kind of approximations lead to an SCR-like ansatz. In this way, further insight into the validity of the ansatz, concerning both technical details of the calculation as well as the approximate separation of physical mechanisms (shake-off and knock-out), can be obtained.

In [4], a Born series for the transition amplitude from the ground state ψ_i to a final state $\psi_f^{(0)}$ of a two-electron target following single-photon absorption has been derived. It was shown that, under the assumption of negligible electron–electron correlation in the ionized final state, the transition amplitude can be written as

$$a_{fi} = -2\pi \mathrm{i}\delta(E_f - E_i - \omega)\langle\psi_f^{(0)}|\left(1 - \mathrm{i}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}H_0 t} T_{ee} \mathrm{e}^{-\mathrm{i}H_0 t}\right) V_{pe}|\psi_i\rangle. \quad (1)$$

In the above equation, V_{pe} is the photon–electron interaction, usually taken in dipole approximation, H_0 is the final-state Hamiltonian $H_0 = H_{at} - V_{ee}$ and T_{ee} denotes the Coulomb T-matrix for electron–electron scattering. $\psi_f^{(0)}$ is an eigenfunction of H_0, i.e. a product of two one-electron states, due to the assumption of vanishing electron–electron correlation in the final state (where at least one electron is ionized), while ψ_i is the fully correlated initial (ground) state of the target. Introduction of a complete set of intermediate states then allows for a separation (on the *amplitude* level!) of the initial photon absorption from the subsequent propagation

$$a_{fi} = -2\pi \mathrm{i}\delta(E_f - E_i - \omega) \sum\!\!\!\!\!\!\int_a \langle\psi_f^{(0)}|S_+|\psi_a\rangle\langle\psi_a|V_{pe}|\psi_i\rangle, \quad (2)$$

where the notation

$$S_+ \equiv 1 - \mathrm{i}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}H_0 t} T_{ee} \mathrm{e}^{-\mathrm{i}H_0 t} \quad (3)$$

is motivated by its resemblance to a conventional scattering S-matrix. Note, however, that S_+ is not strictly an S-matrix for electron–electron scattering since the time integral in equation (3) is restricted to positive t values, i.e. S_+ corresponds to a *half*-collision. Furthermore, let us choose the complete set $\{\psi_a\}$ in such a way that

$$\psi_{abs}(1,2) \equiv \frac{(V_{pe}\psi_i)}{\sqrt{\langle (V_{pe}\psi_i)|(V_{pe}\psi_i)\rangle}} \tag{4}$$

is contained in this set. From the orthogonality condition for the basis states, all other basis states are then orthogonal to $V_{pe}\psi_i$. Thus the sum over intermediate states in equation (2) collapses to a single term and we can write

$$a_{fi} = -2\pi \mathrm{i}\delta(E_f - E_i - \omega)\langle \psi_f^{(0)}|S_+|\psi_{abs}\rangle\langle\psi_{abs}|V_{pe}|\psi_i\rangle. \tag{5}$$

The photon absorption probability is then given by a sum over all final states $\psi_f^{(0)}$ of the transition probability per unit time into the state $\psi_f^{(0)}$

$$P_{abs} = 2\pi \sum_f \delta(E_f - E_i - \omega)|\langle\psi_f^{(0)}|S_+|\psi_{abs}\rangle|^2|\langle\psi_{abs}|V_{pe}|\psi_i\rangle|^2. \tag{6}$$

On the other hand, it is also directly given by

$$P_{abs} = 2\pi \sum_f \delta(E_f - E_i - \omega)|\langle\psi_f|V_{pe}|\psi_i\rangle|^2. \tag{7}$$

(Note that the ψ_f in equation (7) are eigenfunctions of the full atomic Hamiltonian H_{at} including electron–electron interaction, in contrast to the final states in equation (6).) From equation (4), however, it immediately follows that

$$|\langle\psi_{abs}|V_{pe}|\psi_i\rangle|^2 = \langle V_{pe}\psi_i|V_{pe}\psi_i\rangle = \sum_f |\langle\psi_f|V_{pe}|\psi_i\rangle|^2, \tag{8}$$

which in general does not coincide with the expression (7) involving an additional delta function. Hence, it can be seen that it is precisely the off-shell (i.e. off the final-state energy shell) part of ψ_{abs} which prohibits an exact factorization of the transition probability into a photon absorption probability and an 'energy redistribution' part. Note that this can also be seen from equation (2) directly if the set of intermediate states ψ_a is chosen as eigenstates of H_0. Then

$$\langle\psi_f^{(0)}|S_+|\psi_a\rangle = \delta_{fa} - \mathrm{i}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f - E_a)t}\langle\psi_f^{(0)}|T_{ee}|\psi_a\rangle \tag{9}$$

and from

$$\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}(E_f-E_a)t} = \pi\delta(E_f - E_a) + \mathrm{i}\frac{\mathcal{P}}{E_f - E_a} \tag{10}$$

it becomes clear that the off-shell part of ψ_{abs} is a consequence of time ordering [12], i.e. that requiring the photon to be absorbed first restricts the time integral in (3) to positive t values.

For the remainder of this discussion, let us neglect the photon absorption process and focus on the second step of the ionization process, namely the 'half-collision' part of equation (5)

$$a_{f,abs} \equiv \sqrt{2\pi}\delta(E_f - E_i - \omega)\langle\psi_f^{(0)}|1 - \mathrm{i}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}H_0 t}T_{ee}\mathrm{e}^{-\mathrm{i}H_0 t}|\psi_{abs}\rangle. \tag{11}$$

(The splitting of the factor 2π is motivated by the fact that the resulting shake *probability* to be discussed below reduces to the correct asymptotic form at high energies.) $a_{f,abs}$ is seen to consist of two parts, namely the interaction free unity operator '1' and the operator 'T' involving electron–electron interaction. Naturally, the former can be associated with a shake process while the latter corresponds to a 'knock-on' (we use the expressions shake and knock-*on* for any final state and the terms shake-*off* and knock-*out* for doubly ionized states as in SCR). Hence, we propose

$$a^S_{f,abs} \equiv \sqrt{2\pi}\,\delta(E_f - E_i - \omega)\langle\psi_f^{(0)}|\psi_{abs}\rangle \tag{12}$$

as a working definition for the shake amplitude at a finite excess energy $E = E_i + \omega$. However, the shake and knock-on contributions are summed on the *amplitude* level. To arrive at the SCR ansatz, the additional approximation of an incoherent summation of shake and knock-on has to be made[1]. The error introduced by this approximation is at most of the order of the smaller of the two contributions, i.e. it goes to zero in the high- as well as low-energy limit and could only contribute significantly at intermediate energies. Even there it was found in SCR that the error is of the order of a few per cent only (at least for the double-to-single ionization ratio of helium). One would speculate [4, 9] that this is to a large extent due to the population of different final states by the two mechanisms. For shake, for example, the 'shaken' electron will be in an s-state, while the knock-on mechanism will also populate higher angular momentum states. Calculations of angular-differential cross sections should shed further light on this question.

From equation (12), the *probability* for a shake process to a final state $\psi_f^{(0)}$ per unit time is found to be

$$P^S_{f,abs} = \delta(E_f - E)|\langle\psi_f^{(0)}|\psi_{abs}\rangle|^2. \tag{13}$$

With the definition of ψ_{abs}, equation (4), this is more explicitly written in terms of the initial state as

$$P^S_{f,abs} = \delta(E_f - E)\frac{|\langle\psi_f^{(0)}|V_{pe}\psi_i\rangle|^2}{\langle V_{pe}\psi_i|V_{pe}\psi_i\rangle}. \tag{14}$$

This expression differs somewhat from the one given by Åberg [1] (equation (7) of SCR). In contrast to the former, it contains the 'photoabsorption operator' V_{pe}. It seems that the current definition equation (14) is preferable since it arises naturally from the preceding arguments: the sudden approximation underlying the shake-off picture is with respect to the electron–electron interaction, not with respect to the photon absorption. As noted by SCR, if the photoelectron is in an s-state initially, it will be in a p-state after absorption of the photon. That is, to the extent that the dipole approximation is valid for the photon–electron interaction and that the single-particle angular momentum l is a good quantum number, the ψ^ν defined by Åberg is identically zero. It should be noted, however, that both expressions lead to the same high-energy limit. In this limit, $\langle\psi_f^{(0)}|\psi_i\rangle$ as well as $\langle\psi_f^{(0)}|V_{pe}\psi_i\rangle$ both become proportional to $\langle\phi_{\epsilon_f}(\boldsymbol{r}_1)|\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2 = 0)\rangle$ (where ϕ denotes the one-electron state of the shaken electron and ϵ its energy) with different prefactors. Since they appear equally in the numerator and the denominator of (14) they cancel out, leading to the same high-energy limit. The same is true for *all* energies if, as in SCR, product wavefunctions are used for the initial state, or if the PEAK approximation is employed [4, 7, 9], i.e. if the absorption of the photon is assumed to happen always at the nucleus at any excess energy E. In this case one arrives at the 'natural' definition (equation (8) of SCR)

$$P^S_{f,abs} = \theta(E - \epsilon_f)|\langle\phi_{\epsilon_f}|\phi_i\rangle|^2 \tag{15}$$

(where θ is the unit step function), i.e. the overlap of two one-electron wavefunctions. (In the case of using the PEAK approximation for a correlated initial state $\phi_i \equiv \psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2 = 0)/\langle\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2 = 0)|\psi_i(\boldsymbol{r}_1, \boldsymbol{r}_2 = 0)\rangle^{1/2}$.)

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[1] In addition to that, the knock-on part has been obtained from a classical CTMC calculation in SCR. While such a treatment is frequently employed in the study of atomic collision processes, an evaluation of its quality is beyond the scope of the present letter.

As argued above, the successful application of the SCR method showing excellent agreement with experiment and *ab initio* calculations suggests the adoption of equation (14) as a good 'operational' definition of shake-off. In this spirit, shake-off may be phrased vaguely as the part of the double ionization that is absent in a full collision (due to the orthogonality of initial and final states), or, more precisely, that part which does not involve an electron–electron interaction explicitly (of course, interaction is implicit in the correlation present in the initial state, without which there would be no shake-off). It should be noted that the quality of this definition depends on the observation that there is very little interference between shake-off and knock-out, as discussed above. The fact that this is not strictly true leads to some problems e.g. at very low energies, where this separation would lead to a linear dependence of the double ionization cross section on the excess energy, in contrast to the well known Wannier threshold power law [13].

On the other hand, one might want to adopt a maybe more 'physical' definition of shake-off on the basis of the intuitive picture of a time dependence of the effective one-electron potential the 'shaken' electron feels. For asymptotically high energies, it is the sudden change of this potential that leads to a relaxation of the electron which is not in an eigenstate anymore after the potential has changed. In this sense, the change in the effective potential does not occur suddenly anymore at finite energies, but rather over a timescale given by the velocity of the outgoing photoelectron. This is the basis for the definition of shake-off adopted in [2], where an expression has been derived from time-dependent perturbation theory, and also the rationale behind the somewhat *ad hoc* formulation used in [4] which is motivated by a Rosen–Zener-like expression for diabatic transition probabilities familiar from ion–atom collisions. It should be noted that, in contrast to (14), both of these expressions show an exponential decrease towards threshold, so that the Wannier threshold law is recovered. While in the SCR-expression the probability to be shaken into a specific final state does not depend on the rate of change of the potential (i.e. the velocity v of the photoelectron) as long as it is energetically allowed, this is different in [2, 4] where these probabilities depend exponentially on v^2 and v, respectively. In view of these differences, it is surprising to see that the numerical values resulting from these different definitions are in fact rather similar, as is demonstrated in figure 1. This leads us to suggest (14) as a good working definition of shake-off at finite energies. It agrees qualitatively with other natural and maybe more 'physical' definitions and, moreover, it has been shown to lead to a very good approximate separation of mechanisms into shake-off and knock-out. It is easy to calculate and, as compared to [2, 4], has the advantage that it does not contain any free parameters (such as a characteristic range of interaction as in [2] or an effective impact parameter as in [4]). However, one should always keep in mind that the significance of (14) as an independent physically meaningful quantity is limited, as discussed, e.g., in connection with the behaviour of the cross section near threshold.

At this point, a short comment on a comparison with other available definitions of shake-off seems to be in place. So far we have given a comparison with [2, 4] only, and used the qualitative agreement with the values calculated from the expressions given there as an argument in favour of the current definition. However, as argued before, some other definitions found in the literature lead to shake-off values rather different from the present. The shake-off calculated from many-body perturbation theory (MBPT) [3], for example, is found to have a completely different behaviour. Its shape (as a function of energy) as well as the high-energy limit reached, even the answer to the question whether it is the dominant process at high energies or not, depend on the choice of the gauge in which the corresponding diagram is calculated. This is not too surprising in view of the fact that only the sum of all first-order diagrams (shake-off plus ground-state correlation plus two-step one) has a well defined and gauge invariant meaning. Hence, the meaning of shake-off is well defined within MBPT;

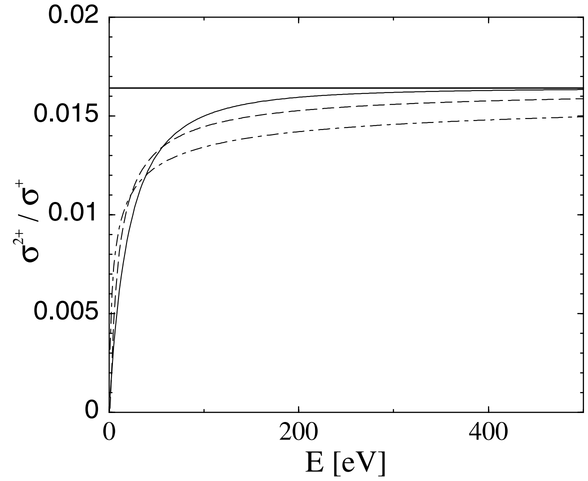

Figure 1. Comparison of different shake-off expressions in the case of the helium ground state. Solid curve, [7]; dashed, [2]; dot–dashed, [4]; the thick solid line shows the asymptotic $E \to \infty$ limit.

however, it is not claimed to have any independent physical meaning of its own. In this sense, it is not a helpful quantity if one wishes to discuss approximate physical mechanisms. Another definition, originally formulated by Åberg [1], has recently been used by Shi and Lin [6] to calculate shake-off double ionization of the helium ground state. Their result for the double-to-single cross section ratio is found to be significantly larger than the latest experimental data for the *total* ratio, i.e. including all possible decay routes (e.g. shake-off and knock-out). From [6] it is not entirely clear how much of this 'overshooting' has to be attributed to a poor choice of the ground-state wavefunction (leading to an asymptotic high-energy limit which is somewhat too large) and how much would still be observed using a more accurate initial state. Assuming that this effect persists it would be obvious that again no physical meaning can be ascribed to this definition of shake-off, since shake-off alone would already be larger than the sum of all mechanisms. In any case, a further discussion would have to await a corresponding formulation of 'non-shake-off', since it is only the sum of all possible ionization mechanisms which can directly be compared with experiment. Finally, Kheifets [5] has proposed a definition of shake-off where the diagonal part of the T-matrix contribution to the convergent close-coupling model is absorbed into shake-off. In his calculations for helium, it was found that with this definition of shake-off the total cross section ratio approaches the shake-off value quickly, and non-shake-off becomes negligible at about 100 eV of excess energy. However, the last panel of figure 2 of [5] shows that for lower energies shake-off alone again exceeds the total ratio. Hence, once more one has to conclude that the meaning of shake-off as defined in [5] as an independent physical mechanism is limited.

In summary, we have argued that no unique definition for shake-off at finite energies exists. Nevertheless, we propose equation (14) as a good 'operational' definition. Clearly, when shake-off at finite energies is discussed (in particular in the sense of an approximate physical mechanism in connection with experiments), care has to be taken with the precise meaning of the term, i.e. its actual definition adopted in each case. In addition to our discussion of shake-off, we have indicated a way towards a rigorous derivation of the SCR ansatz for calculation of double ionization by relating it to a perturbation expansion starting from a full quantum mechanical point of view.

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