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Core-excitation effects in multiphoton processes

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The question of whether the central-field approximation is a suitable vehicle for accounting for core-excitation effects is revisited. It is concluded that the errors that this model makes in inner-shell excitation energies can be smaller than suggested by Crance and Aymar [J. Phys. B **20**, L155 (1987)].
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An issue that has arisen from time to time in the construction of perturbative theories of multiphoton transitions is that of correctly accounting for core-excitation effects [1–5]. In most cases, inner-shell contributions in processes excited by infrared or optical radiation are negligible. Exceptions occur, for example, in very strong fields, where one may be concerned with multiple ionization and/or excitation, and where core effects involve the very essence of the problem. In addition, even in the weak-field regime, they may become significant if short wavelengths are involved, or, similarly, at long and intermediate wavelengths, if there are virtual state resonances at high harmonics of the driving frequency. In this paper, we are concerned with properly treating the influence of occupied inner shells on n-photon transitions of the outermost electrons, with particular emphasis placed on taking account of the Pauli principle. (Related questions arose in a calculation reported by Guo [6], who studied two-photon x-ray emission in purely inner-shell processes.) We shall resume earlier discussions of this matter [2–5] and address the assertion [5] that the central-field, independent-particle approximation is a poor model to use if one wished to accurately account for core excitations. We follow our earlier work [3], and restrict the discussion to the simplest multiquantum processes, two-photon absorptions at a single frequency. The extension to emission processes, a larger number of photons and more than one color can be readily made.

As was noted in our previous paper [3], the amplitude M for a two-photon process between atomic states in which a valence electron undergoes a transition from orbital μ to orbital σ is given by

$$M=\Sigma_1+\Sigma_2, \tag{1}$$

where

$$\Sigma_1=\Sigma_i\langle f|d_{i\sigma}d_{\mu i}a_\sigma^+a_ia_i^+a_\mu|0\rangle/(E_\mu-E_i+E_p), \tag{2}$$

$$\Sigma_2=\Sigma_I\langle f|d_{I\sigma}d_{\mu I}a_I^+a_\mu a_\sigma^+a_I|0\rangle/(E_I-E_\sigma+E_p). \tag{3}$$

Equation (2) represents the ‘‘ordinary’’ summation of second-order perturbation theory—it spans all intermediate states in which the valence electron is coupled to an orbital i that is vacant in $|0\rangle$. The summation in Eq. (3) represents contributions from core states; an inner electron in orbital I is excited to σ (occupied in the final state) in the first half of the transition, while, in the second half, the valence electron in orbital μ recombines with the hole in orbital I that had been created in the core. As was demonstrated [3], the combination of Σ_1 and Σ_2 is equivalent to a summation possessing the form of Σ_1 alone, but where i now includes orbitals occupied in $|0\rangle$, in addition to the vacant ones. This scheme of ignoring both the Pauli principle and the core excitations is the analog, in transition amplitude calculations, of exclusion-principle-violating terms in energy calculations.

The chief motivation for combining the two classes of intermediate states into a single summation is that doing so enables one to exploit the inhomogeneous equation procedure (sometimes called ‘‘implicit summation) [1,7–9] with an atomic model that involves only the outermost electron—i.e., the problem is reduced to a one-body system. To apply this method, one solves an inhomogeneous Schrödinger equation for a particle moving in a fixed static potential, obtaining a function Ψ_1, and determines the single matrix element between it and the final-state wave function of the charge-field coupling operator. The transition amplitude obtained this way is identical to that determined by the more familiar route of performing an infinite summation. It avoids both the need either to calculate a large number of terms and superimpose them, or find a trick to resum the indicated series exactly. In principle, the technique is valid in all problems—the question in particular cases is whether one can solve the differential equations. The relevant equations are easy to integrate numerically when the unperturbed system is described in the independent-particle, central-field model, since they are separable. The equivalent calculation is much more difficult to perform in more accurate models which do not separate. For those cases, where the inhomogeneous equations can be integrated, the method is actually easier to apply than the more conventional infinite sum approach.

We now arrive at the point of divergence between Crance and Aymar [5] (CA) and the present author. While CA agreed that the *formalism* described above is correct, they asserted that inner-shell excitation energies predicted by typical independent particle approximation (IPA) potentials are not accurate enough to allow them to be used reliably in practical calculations of transition amplitudes. Thus their objection is actually to calculations which utilize the single-particle energies of the IPA rather than to the particular way that the IPA is implemented. To remedy this defect in the IPA, they proposed that the occupied shells be projected out of the solution to the inhomogeneous Schrödinger equation, and their contributions calculated separately by some other

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method, which presumably correctly takes account of the core excitation energy. Thus CA supported similar suggestions made by Baroni and Quattropani [2] and Laplanche and Jaouen [4]. To validate their arguments, CA provided a list comparing energy denominators taken from matrix element summations for alkali atoms in the IPA with what they claimed are experimental values of the same parameters, and concluded that major discrepancies exist between the two.

If CA were correct that there exist major disagreements between experimental and IPA core-excitation energies, their conclusion would also be valid; transition amplitudes calculated via single-particle inhomogeneous Schrödinger equations would not be reliable insofar as core contributions are concerned, and one would be obliged to adopt a scheme such as they suggested for improving the level of accuracy.

There are two issues that appear here. First is the question of the particular central field model chosen by CA. The second is the way that the ''experimental data'' are chosen. We discuss the second point first. Examination of the ''observed energy defects'' presented by CA reveals that they used term energies of the singly ionized alkali systems, which are, of course, the bound systems remaining after the transition has occurred. It is questionable, however, whether these ionic term values are the correct ones for describing the neutral system. The present author believes that one should use inner-shell ionization energies for neutral atoms, the systems actually being irradiated.

There is a transparent argument that seems to demonstrate this point. Consider the particular case where the photon energy lies at the threshold for two-photon ionization (of the valence electron). Then $E_\sigma = 0$, and the only particle parameter remaining in the denominator of Eq. (3) is E_I, which therefore represents the negative of the minimum energy to ionize core orbital I and leave the valence electron(s) with its (their) original quantum numbers. We immediately see that the E_I represent the inner-shell binding energies for the neutral atoms, and we must correctly identify which published parameters they are.

That these are the neutral atom term energies follows from Koopmans' theorem (Bethe and Jackiw [10], Gross, Runge, and Heinonen [11]), which asserted that experimental ionization energies of given electronic levels are (approximately) equal to the corresponding one-body eigenvalues found in solving the Schrödinger equation for the neutral atom in the Hartree-Fock approximation. Many other versions of the central field model predict similar energies, for example, the Slater free-electron-hole approximation to Hartree-Fock [12] or any minor modification thereof.

The general conclusion drawn from Koopmans' theorem that Hartree-Fock eigenvalues approximate binding energies is supported by the values of spectroscopic intervals [13] between the alkali-metal ground $(n-1)p^6ns$ states and the configurations $(n-1)p^5ns^2$, especially in the heavier elements K, Rb, and Cs. (Moore did not provide the excitation energies of the analogous p^5s^2 states in Na. In the heavier alkalis the states of interest are actually fairly highly excited Feshbach resonances or autoionizing states rather than true bound levels.)

This does not mean that *all* central field models are equally good for approximating term energies. The Klapisch [14] model, which represents the basis for the attack by CA on the central-field approximation, seems to be particularly poor in this regard, however, and one should not accept conclusions based on it as typical.

TABLE I. Theoretical and experimental energies (in Ry) of $(n\text{-}1)p^5ns^2$ configurations in heavier alkali metals. Experimental values are taken from Moore's tables, and represent statistical averages of $j=\frac{1}{2}$ and $\frac{3}{2}$ states. Theoretical values are obtained from one-electron energies of Klapisch[a] and the Hartree-Fock-Slater tables of Herman and Skillman.[b]

System	K	Rb	Cs
Theory[a]	1.1546	0.8724	0.5916
Theory[b]	1.4242	1.1870	0.9923
Experiment	1.3821	1.1461	0.9343

Table I lists the indicated configuration-averaged excitation energies from Moore, together with those calculated by the Hartree-Fock-Slater (HFS) method (Herman and Skillman [12]) and in the central field model used by CA (Klapisch [14]) to find inner-shell term values. The Klapisch energies are obtained by subtracting the relevant photon energy from the denominator quoted by CA. The discrepancies between the calculated HFS one-electron energy differences and the observed term values are much smaller than the errors that would be present if CA were correct in identifying core-excitation energies with ionic transitions. We also note that if the ionic energies were the appropriate ones to use, Koopmans' theorem would be incorrect. The Klapisch energies compare poorly with the neutral transition energies, and, of course, the differences between Klapisch and ionic transition energies are even worse. In effect, the opposite signs of the errors, due to a poor theoretical model and term values for the wrong system, generates the illusion of a theory-experiment disagreement which is not present.

Even though the experimental inner-shell energies for the neutral systems are closer than their ionic counterparts to the values predicted by a good central-field model, agreement is not perfect, and one may wish to modify the independent-particle Hamiltonian chosen for the problem to make the theoretical energies correspond more closely to the experimental values for the neutral situation. Since the existing discrepancies are small, this can be accomplished by appending terms containing adjustable coefficients to the static potential interacting with the electrons, a procedure used, for example, in Refs. [1,15].

We should also emphasize that it is not incorrect to project the occupied states out of Φ_1 and calculate Σ_2—merely that it is redundant to do so, since the labor involved in such calculation would be wasted, as the results of the two steps exactly cancel. It is also true, of course, that central field models are not exact, even if the potential is adjusted to make energies agree with observation, and one cannot expect to find perfect agreement between it and experiment for transition probabilities. In this regard, one may use the Hartree-Fock approximation or a similar one as the first step in a sequence of calculations where the difference between the true and central-field potentials is taken into account perturbatively.

Thus we conclude that one cannot choose an arbitrary central-field atomic model for multiphoton ionization when inner-electron effects are taken into account, but should, at a minimum, select a description which incorporates energy-level values close to experiment. Because of Koopmans' theorem, eigenfunctions and eigenvalues computed in the Hartree-Fock and similar approximations serve well for this purpose. The relevant ''experimental term values'' for this purpose must be appropriate for the initial state of interest, not the ionized final state.

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