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Velocity- and length-form relations in two-electron single-photon transitions

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It is shown that the usual length-form approximation to the momentum matrix element $(m/i\hbar)(E_i-E_f)\langle f\,|\,\mathbf{R}\,|\,i\rangle$, although correct for the usual single-electron single-photon transitions, is off by about a factor of 2 for two-electron single-photon transitions in the x-ray region. A much more accurate result is obtained if the total atomic-energy difference E_i-E_f is replaced by the single-particle-energy difference of the electrons involved in the transition (e.g., $E_{2p}-E_{1s}$).

INTRODUCTION

Atomic transitions in which two electrons change states while emitting only a single photon were first discussed many years ago.[1] Recently, there has been renewed interest in this phenomenon because of the discovery of such transitions in the x-ray region.[2] There have also been several theoretical papers[3] which calculate relative transition rates yielding results in rough agreement with the experimental results of Wölfli *et al.*,[2] but at great variance with those of Salem *et al.*[2]

With the possible exception of Kelly,[3] these calculations all make use of the length form[4,5] of the interaction matrix element. The relative accuracy of the length, velocity, and acceleration forms has been discussed before in the literature,[6] but never in the context of two-electron single-photon transitions.

The purpose of this paper is to point out that the usual calculations using the length approximation and experimentally determined transition energies yield a result (for relative transition probabilities) too large by about a factor of 4 for two-electron single-photon transitions and that a simple remedy is available.

CALCULATION

The theory of radiation[7] requires the calculation of the matrix element T

$$T=\langle f\,|\,\mathbf{P}_q\,|\,i\rangle\ , \tag{1}$$

where $|\,i\rangle$ and $|\,f\rangle$ are completely antisymmetric state vectors for the initial and final states, respectively, and $\mathbf{P}_q$ is defined by Eq. (2) as

$$\mathbf{P}_q=\sum_{i=1}^{N}\mathbf{p}_q(i)\ . \tag{2}$$

$\mathbf{p}_q(i)$ is the qth component of the momentum operator of particle i. By noting that

$$\frac{i\hbar}{m}\mathbf{P}=[\mathbf{R},H]\ , \tag{3}$$

where H is the Hamiltonian of the system (excluding the interaction with the radiation field), and

$$\mathbf{R}=\sum_{i=1}^{N}\mathbf{r}(i) \tag{4}$$

with $\mathbf{r}(i)$ being the position operator of the ith particle, one can easily show that

$$\frac{i\hbar}{m}\langle f\,|\,\mathbf{P}\,|\,i\rangle=(E_i-E_f)\langle f\,|\,\mathbf{R}\,|\,i\rangle\ , \tag{5}$$

where

$$H\,|\,i\rangle=E_i\,|\,i\rangle \text{ and } H\,|\,f\rangle=E_f\,|\,f\rangle\ . \tag{6}$$

The relation shown in Eq. (5) is exact if exact eigenfunctions are used. In practice, however, approximate eigenfunctions are nearly always used so that different results are obtained depending upon whether the left-hand side (velocity form) or the right-hand side (length form) of Eq. (5) is used. The length form is usually chosen because it is easier to calculate.

We restrict our considerations to calculations of the Hartree-Fock type in which the state vectors are represented by single-configuration angular-momentum-coupled uncorrelated state vectors. In this approximation, the two-electron single-photon transitions can only occur if the final-state vectors are computed from a different approximate Hamiltonian than was used to compute the initial-state vector. We separate the exact Hamiltonian into an uncorrelated part H_0 and the remainder V. Primes will be used to denote final-state quantities,

$$H=H_0+V=H_0'+V'\ , \tag{7}$$

$$H_0=\sum_{j=1}^{N}H(j);\ \ H_0'=\sum_{j=1}^{N}H'(j)\ . \tag{8}$$

The notation we shall follow is as follows: primed quantities refer to the Hamiltonian H_0' appropriate to the final state of the system, whereas unprimed quantities refer to eigenfunctions of H_0 (the initial state). $H(j)$ can be considered to be an effective single-particle Hamiltonian which contains in addition to the kinetic energy and the nuclear Coulomb potential, a self-consistent configuration-dependent potential function which represents the interaction with the other electrons. Such a potential is the basis of the Hartree-Fock-Slater method.[8] Distinct letters refer to distinct sets of quantum numbers, e.g., a, b, etc., but $|a\rangle$ and $|a'\rangle$ refer to the eigenfunctions of H_0 and H_0', respectively, having *identical* quantum numbers a and somewhat different energies E_a and E_a'.

Upon noting that $\mathbf{R}$ commutes with V and V', Eq. (3) can be rewritten

$$\frac{i\hbar}{m}\mathbf{P}=\mathbf{R}H_0-H_0'\mathbf{R}+(V-V')\mathbf{R}\,. \tag{9}$$

We now identify $|i\rangle$ and $|f'\rangle$ as solutions of the Hartree-Fock-Slater Hamiltonians of Eq. (8) with energy eigenvalues E_i and E_f', and Eq. (9) becomes

$$\frac{i\hbar}{m}\langle f'|\mathbf{P}|i\rangle=(E_i-E_f')\langle f'|\mathbf{R}|i\rangle+\langle f'|(V-V')\mathbf{R}|i\rangle\,. \tag{10}$$

This is the relation ordinarily used when the last term is neglected. Although this term is small for single-electron single-photon transitions, it is *not* small for the two-electron single-photon transitions under consideration here. Equation (10) may be reduced to a single-particle matrix element using the usual methods of Racah algebra. We note that the initial and final states differ only in two sets of single-particle quantum numbers and we assume (a good approximation) that the initial- and final-particle states having identical quantum numbers have overlap integrals of one. A useful model to keep in mind might be $2p^6 2s^2\to 2p'^5 2s' 1s'^2$ where $\langle 2p'|2p\rangle\approx 1$, $\langle 2s'|2s\rangle\approx 1$, and $\langle 1s'|2s\rangle\neq 0$ because the initial and final Hamiltonians are different. Let us assume that the initial and final states differ by the single-particle quantum numbers $a\to\alpha$ and $b\to\beta$, where $|a\rangle$ is orthogonal to $|\beta\rangle$ and $|b\rangle$ to $|\alpha\rangle$. In our model, $a=2s$, $\alpha=1s$, $b=2p$, and $\beta=1s$, so that $a\to\alpha$ corresponds to the $2s\to 1s$ transition and $b\to\beta$ to the $2p\to 1s$,

$$\langle f'|\mathbf{P}|i\rangle=A\langle\alpha'|a\rangle\langle\beta'|\mathbf{p}(1)|b\rangle\,, \tag{11}$$

where the factor A contains the details of the configuration and angular-momentum coupling, $\langle\alpha'|a\rangle$ is the overlap integral for one of the electrons (e.g., $\langle 1s'|2s\rangle$ in our example), and $\langle\beta'|\mathbf{p}(1)|b\rangle$ is the single-particle momentum matrix element evaluated using the (arbitrarily chosen) coordinates of particle one. This matrix element can also be written in length form using

$$\begin{aligned}\frac{i\hbar}{m}\mathbf{p}(1)&=[\mathbf{r}(1),H]=[\mathbf{r}(1),H_0]\\&=\mathbf{r}(1)H(1)-H'(1)\mathbf{r}(1)\\&\quad-[H(1)-H'(1)]\mathbf{r}(1)\,,\end{aligned} \tag{12}$$

where we have used the fact that $[\mathbf{r}(1),V]=0$ and $[\mathbf{r}(1),H(i)]=0$ for $i\neq 1$. We can now insert the operator appearing in Eq. (12) between single-particle states:

$$\begin{aligned}\frac{i\hbar}{m}\langle\beta'|\mathbf{p}(1)|b\rangle&=(E_b-E_\beta')\langle\beta'|\mathbf{r}(1)|b\rangle\\&\quad+\langle\beta'|[H'(1)-H(1)]\mathbf{r}(1)|b\rangle\,.\end{aligned} \tag{13}$$

In order to compare this expression with Eq. (10), we first express Eq. (10) in terms of single-particle matrix elements. Since $\mathbf{R}$ is a symmetric sum of single-particle vector operators, as is $\mathbf{P}$, Eq. (11) holds with $\mathbf{P}$ replaced by $\mathbf{R}$ and $\mathbf{p}$ by $\mathbf{r}$. From Eq. (10) one can also see that the same must be true for the last term. We wish to cast this term into a form whose magnitude can be estimated:

$$\begin{aligned}\langle f'|(V-V')\mathbf{R}|i\rangle&=\langle f'|(H_0'-H_0)\mathbf{R}|i\rangle\\&=E_f'\langle f'|\mathbf{R}|i\rangle-\langle f'|H_0\mathbf{R}|i\rangle\,.\end{aligned} \tag{14}$$

The last term in Eq. (14) can be transformed by noting that

$$H_0\mathbf{R}=\mathbf{R}H_0+\sum_{j=1}^{N}[H(j),\mathbf{r}(j)]\,, \tag{15}$$

so that Eq. (14) becomes

$$\begin{aligned}\langle f'|(V-V')\mathbf{R}|i\rangle&=(E_f'-E_i)\langle f'|\mathbf{R}|i\rangle\\&\quad-\sum_{j=1}^{N}\langle f'|H(j)\mathbf{r}(j)|i\rangle\\&\quad+\sum_{j=1}^{N}\langle f'|\mathbf{r}(j)H(j)|i\rangle\,.\end{aligned} \tag{16}$$

The operators on the right-hand side of Eq. (16) are all symmetric sums of single-particle vector operators and, thus, may be reduced to the form of Eq. (11). Equation (16) then becomes

$$\begin{aligned}\langle f'|(V-V')\mathbf{R}|i\rangle=A\langle\alpha'|a\rangle[&(E_f'-E_i)\langle\beta'|\mathbf{r}(1)|b\rangle\\&+\langle\beta'|\mathbf{r}(1)H(1)|b\rangle\\&-\langle\beta'|H(1)\mathbf{r}(1)|b\rangle]\,.\end{aligned} \tag{16'}$$

If we then use Eq. (11) and the above expression, Eq. (10) may be written in single-particle form,

$$\frac{i\hbar}{m}\langle\beta'|\mathbf{p}(1)|b\rangle=(E_i-E_f')\langle\beta'|\mathbf{r}(1)|b\rangle+R_1 \tag{17}$$

(approximation A), where

$$\begin{aligned}R_1&=(E_f'-E_i)\langle\beta'|\mathbf{r}(1)|b\rangle+\langle\beta'|\mathbf{r}(1)H(1)|b\rangle\\&\quad-\langle\beta'|H(1)\mathbf{r}(1)|b\rangle\\&=(E_f'-E_i+E_b)\langle\beta'|\mathbf{r}(1)|b\rangle\\&\quad-\sum_{c}\langle\beta'|H(1)|c\rangle\langle c|\mathbf{r}(1)|b\rangle\,,\end{aligned} \tag{18}$$

where $|c\rangle$ is a member of the complete set of eigenfunctions of $H(1)$. Using this, one can rewrite Eq. (18) as follows:

$$\begin{aligned}R_1&=(E_f'-E_i+E_b)\langle\beta'|\mathbf{r}(1)|b\rangle\\&\quad-\sum E_c\langle\beta'|c\rangle\langle c|\mathbf{r}(1)|b\rangle\,.\end{aligned} \tag{19}$$

The overlap integrals $\langle\beta'|c\rangle$ will be nearly zero unless the sets of quantum numbers β and c are the same; thus, only the single term need be kept, and R_1 is accurately given by

$$R_1=(E'_f-E_i+E_b-E_\beta)\langle \beta \,|\, \mathbf{r}(1) \,|\, b \rangle \ , \tag{20}$$

where we have also assumed that $\langle \beta' \,|\, \mathbf{r}(1) \,|\, b \rangle = \langle \beta \,|\, \mathbf{r}(1) \,|\, b \rangle$.

For our example $2p^6 2s^2 \rightarrow 2p'^5 2s' 1s'^2$; $E_b=E_{2p}$, $E_\beta=E_{1s}$, $E'_{1s} \simeq E_{1s}$, and $E'_f-E_i \simeq 2E_{1s}-E_{2p}-E_{2s}$, so that $R_1 \simeq (E_{1s}-E_{2s})\langle 1s \,|\, \mathbf{r}(1) \,|\, 2p \rangle$. In the usual approximation,[4] this term, R_1, is neglected in Eq. (17) which corresponds to neglecting the second term on the right-hand side of Eq. (10).

We shall now show that a much more accurate approximation can be made by calculating the momentum matrix element in a somewhat different fashion. Rather than starting with the many-body formalism and relating the velocity form to the length form using the entire Hamiltonian, as was done in obtaining Eq. (10), one can relate the two on the single-particle level and then work back up to the many-body expression,

$$\begin{aligned}\frac{i\hbar}{m}\mathbf{p}(1)&=[\mathbf{r}(1),H]=[\mathbf{r}(1),H(1)]\\&=\mathbf{r}(1)H(1)-H'(1)\mathbf{r}(1)\\&\quad+[H'(1)-H(1)]\mathbf{r}(1) \ .\end{aligned} \tag{21}$$

From this, one easily obtains

$$\frac{i\hbar}{m}\langle \beta' \,|\, \mathbf{p}(1) \,|\, b \rangle=(E_b-E'_\beta)\langle \beta' \,|\, \mathbf{r}(1) \,|\, b \rangle+R_2 \tag{22}$$

(approximation B) where

$$\begin{aligned}R_2&=\langle \beta' \,|\, [H'(1)-H(1)]\mathbf{r}(1) \,|\, b \rangle\\&=E'_\beta\langle \beta' \,|\, \mathbf{r}(1) \,|\, b \rangle-\sum_c \langle \beta' \,|\, H(1) \,|\, c \rangle\langle c \,|\, \mathbf{r}(1) \,|\, b \rangle \ .\end{aligned} \tag{23}$$

Using similar arguments as were used in deriving Eq. (20), we have

$$R_2=(E'_\beta-E_\beta)\langle \beta' \,|\, \mathbf{r}(1) \,|\, b \rangle \ . \tag{24}$$

For our example $E'_\beta=E'_{1s}$ and $E_\beta=E_{1s}$ so that $E'_\beta-E_\beta=E'_{1s}-E_{1s}$ which is ordinarily very small especially when compared with the remainder term R_1 of Eq. (20).

Thus we see quite clearly that for two-electron single-photon transitions, approximation B [Eq. (22)] is a much better estimate of the momentum matrix element than is approximation A [Eq. (17)]. The complete atomic-energy differences $(E_i-E'_f)$ are much larger than the energy change of the electron involved in the dipole matrix element $(E_b-E'_\beta)$ because of the concomitant energy change of the second electron, so the two approximations differ greatly, with approximation B being much more accurate. In the usual single-electron single-photon transition, the two energy changes are the same and the two approximations become identical. If we consider the example $2p^6 2s^2 \rightarrow 2p'^5 2s' 1s'^2$, then

$$\begin{aligned}&E_i-E'_f=E_{2p}+E_{2s}-2E'_{1s} \ ,\\&E_b-E'_\beta=E_{2p}-E'_{1s}\approx\tfrac{1}{2}(E_i-E'_f) \ ,\end{aligned} \tag{25}$$

where in the final step we have assumed $E_{2p} \approx E_{2s}$. Thus we see that approximation A overestimates the matrix element by a factor of 2 which leads to transition rates too large by a factor of 4. This factor of 4 persists when the branching ratio of two-electron to single-electron transitions is being computed.

We have chosen here to view the two-electron single-photon transition from the "shake-down" model point of view.[9] That is, a nonzero transition rate arises due to the nonvanishing of the overlap integral of the nonradiating transition electron because a different Hamiltonian is used for the final states than for the initial states. In a sense, this introduces some electron correlations into the problem. There is another way to proceed, however, by using a multiconfigurational Hartree-Fock-Slater calculation. In this method, the transition would be allowed as a single-particle transition between small admixtures into the primary configuration. For example, one might have a mixture of $2p^6 2s^2$ and $2p^6 2s\, 1s$, the second component then being capable of making a single-particle transition to the final state, $2p^5 2s\, 1s^2$. From this point of view, it is still imperative that Eq. (17) (approximation A) not be used, at least until the calculation has been reduced to that of a single-particle transition $(2p^6 2s\, 1s \rightarrow 2p^5 2s\, 1s^2)$ at which point both approximations would give the same result.

The results obtained above were based on Eqs. (7) and (8) which require that the Hamiltonian of the system be expandable into a sum of single-particle Hamiltonians with appropriate commutation properties. Hamiltonians of the Hartree-Fock-Slater type have this property and our results clearly apply to such problems. Although Hartree-Fock calculations are more complicated, appropriate single-particle Hamiltonians can be defined, at least for single-configuration average energy calculations.

TABLE I. Single-particle reduced-momentum matrix element $(i\hbar/m)\langle 1s' \| p^{(1)} \| 2p \rangle$ calculated using Hartree-Fock wave functions. Approximation A is from the right-hand side of Eq. (17) (neglecting R_1), while approximation B is from the right-hand side of Eq. (22) (neglecting R_2). All quantities are in atomic units.

		Length form	
	Velocity form	Approximation B	Approximation A
Neon	3.66	3.38	6.97
Calcium	8.39	7.98	16.2
Iron	11.2	10.8	21.9
Copper	12.6	12.2	24.7

(The resulting potentials would have infinite singularities at each of the zeros of the corresponding radial wave functions and would have little practical use.)

To illustrate the applicability of these results to single-configuration Hartree-Fock calculations, we have calculated[10] the velocity form of the single-particle reduced matrix element $(i\hbar/m)\langle 1s' || p^{(1)} || 2p \rangle$ for several elements. The results are displayed in Table I along with the length-form results using approximations A and B. Clearly, the velocity form must be used for accurate results. However, if the length form is desired, then one should use approximation B.

CONCLUSION

The usual method of relating velocity to length formulations of the momentum matrix element in self-consistent field calculations is given by Eq. (17) (approximation A). Although this is correct for the usual single-electron single-photon transitions, it is in error by about a factor of 2 for recently observed two-electron single-photon x-ray transitions and produces an error by a factor of 4 in the transition rates. A better estimate [approximation B of Eq. (22)] is easily obtained by using the single-particle energy change corresponding to the transition matrix element rather than the full atomic-energy changes.

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