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An alternative formulation of the Judd–Ofelt theory of f↔f transitions

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Abstract

A contribution is made to the discussion about the choice between length and velocity formulae which describe the interaction between matter and a radiation field. The analysis is illustrated by the Judd–Ofelt theory of one-photon electric dipole transitions between the levels of $4f^N$ configuration of rare earth ions in crystals. The standard effective operators which contribute to the transition amplitude are one-particle tensor operators of even rank and are defined within the electric gauge of an electromagnetic field. When the radiation gauge is applied, the transition amplitude is determined by new effective operators which are of odd rank. The latter are one-, two- and three-particle objects and are caused by the non-local character of the Hartree–Fock potential of the zeroth-order hamiltonian defined within the central field approximation. The new effective operators are expressed in terms of the so-called perturbed functions; it is demonstrated that their angular factors and radial terms are of the same general structure as in the case of effective operators of the standard Judd–Ofelt theory.

Keywords: Judd–Ofelt theory

1. Introduction

In general there are three different forms of the matter–radiation field interaction. In practice, however, only two of them, the length and velocity forms, are used. These formulae are equivalent if the matrix element of the transition operator is evaluated for exact wavefunctions of the initial and final states involved in a process. Thus there is an arbitrary choice between these two formulations only in the case of one-electron systems or, more generally, in the case of all approaches which are based on the independent particle model. If the description of the energy states goes beyond this crude approximation and electron correlation effects (at least at the level of the Hartree–Fock method) are taken into account, the two forms of interaction usually give different transition amplitudes. It should be pointed out that the possible agreement between the two forms can only be accidental; if this happens, it should not be taken as a criterion of the quality of functions used for evaluation of appropriate matrix elements. Actually, as stated by Starace [1]: "there are cases in which length and velocity formulas using improved wave functions differ by factor of 2 and yet either would be more accurate than central-field-model calculation, in which all alternative formulas give the same result".

The classification of the various approximations introduced in the theory of electric dipole processes is presented in Ref. [1]. Theoretical analyses as well as the results of calculations have proved [1,2] that in the case of all approximate models for which the exact wavefunctions are available, the length formula is the correct one. It is interesting to note also that Amusia et al. found [2] that in the case of methods which are based on the non-local hamiltonian, better agreement with experiment is obtained when the length form is used.

Methods for which the length form has been found to be preferable involve the Hartree–Fock approach, although, owing to the non-local character of the potential, some extra terms have to be introduced. The latter is necessary in order to reach equivalence between the length and velocity forms. The discrepancy between them is a "measure" of the non-locality of the Hartree–Fock potential rather than evidence of the poor quality of the wavefunctions. This aspect is discussed in the present paper in the context of the Judd–Ofelt theory [3,4] of electric dipole transitions between the energy levels of rare earth ions in crystals.

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The main aim of the present paper is to introduce new effective operators which are responsible for the difference between the transition amplitude defined within the standard Judd–Ofelt theory and its version based on the velocity formula.

2. Consequences of non-locality of the hamiltonian

The non-local potential (such as the exchange operator of the Hartree–Fock approach) is not diagonal in the coordinate representation and is defined through its action upon the function in the following way:

$$\langle\vec r|V|f\rangle = \int\langle\vec r|V|\vec r\,'\rangle\langle\vec r\,'|f\rangle \mathrm{d}^3r' \equiv \int V(\vec r, \vec r\,')f(\vec r\,')\mathrm{d}^3r'$$

(while for the local potential we have $\langle\vec r|V|\vec r\,'\rangle = V(\vec r)\,\delta(\vec r-\vec r\,')$). Owing to this property, $V(\vec r, \vec r\,')$ does not commute with the coordinate operator and as a consequence the momentum operator is no longer equivalent to the velocity operator. Actually,

$$\dot{\vec r} = [\vec r, H] = \frac{i\hbar}{\mu}\vec p + [\vec r, V(\vec r, \vec r\,')] \tag{1}$$

where

$$H = h_0 + V(\vec r, \vec r\,') \tag{2}$$

Here h_0 denotes the hamiltonian of, for example, the independent particle model and V is a non-local potential.

The operator H represents the total hamiltonian of a system for which it is possible to solve the eigenvalue problem in an exact way, namely

$$H\Phi_k = E_k\Phi_k, \quad k = 1, 2, \dots \tag{3}$$

The matrix element of Eq. (1) between two different eigenstates of H gives the following equality:

$$(E_k - E_\ell)\langle\Phi_k|\vec r|\Phi_\ell\rangle = \frac{i\hbar}{\mu}\langle\Phi_k|\vec p|\Phi_\ell\rangle + \langle\Phi_k|[\vec r, V(\vec r, \vec r\,')]|\Phi_\ell\rangle \tag{4}$$

It is seen from Eq. (4) that the length form of the electric dipole interaction (the left-hand side of this equality) differs from the velocity version by a term which contains a non-local potential. The last term of Eq. (4) has to be included in order for both forms to be equivalent; this is the term of main interest in the present analysis.

3. Judd–Ofelt theory

3.1. Theoretical background

The one-photon transition amplitude is determined by the first-order term of the time-dependent perturbation expansion performed for the description of a matter–radiation field interaction [5]. In the electric gauge of the electromagnetic field the transition amplitude is proportional to the matrix element of the electric dipole transition operator:

$$\Gamma \approx \langle\Psi_f|D_\rho^{(1)}|\Psi_i\rangle\delta(E_i - E_f \mp \hbar\omega) \tag{5}$$

where Ψ_i and Ψ_f are the wavefunctions of the initial (from which the transition starts) and final (where the process terminates) states. The operator $D_\rho^{(1)}$ in Eq. (5) is the electric dipole operator in the tensorial form

$$D_\rho^{(1)} = \sum_i^N r_i C_\rho^{(1)}(\vartheta_i, \phi_i) \tag{6}$$

The accuracy of calculations based on Eq. (5) depends on the quality of the wavefunctions used for evaluation of the matrix element. If these functions describe the energy levels of the configuration of the equivalent electrons $4f^N$ determined within the central field approximation applied for the free ion, the transition amplitude Γ vanishes owing to parity requirements. This means that as long as the theoretical model is based on the free-ion approximation, one-photon electric dipole transitions between the levels of rare earth ions in crystals are forbidden. However, such transitions are observed in the case of various lanthanides in various hosts. This is evidence then that the theoretical investigations have to be extended beyond the free-ion approximation and that other physical mechanisms have to be considered which might possibly force the one-photon transitions. This means that in reality the parity of wavefunctions of the initial and final states of the discussed systems is not well defined.

Although the optically active 4f electrons of rare earth ions in crystals are well screened from the environment by the closed shells of 5s and 5p symmetry, it is still obvious that the spectroscopic properties of these systems are determined by the crystal field potential. Even if this influence, being rather weak, occurs only in a perturbative way, the components of each wavefunction are of mixed parity; as a consequence, the one-photon transitions are also allowed from a theoretical point of view. This idea has been realized in the papers by Judd [3] and Ofelt [4]. Since there are over 30 years of successful applications of this theory, which in the literature is called the standard theory, it is worthwhile to recapitulate its basic assumptions, advantages and weak points.

The Judd–Ofelt theory is based on the perturbation expansion performed for the following hamiltonian of the ionic system, namely

$$\mathscr{H} = H_0 + \lambda V'_{\mathrm{CF}} \tag{7}$$

where

$$H_0 \equiv H + POP \tag{8}$$

is the unperturbed hamiltonian which consists of two operators: H is from the central field approximation and O represents all such operators which are necessary for a proper description of an ion. P in this definition is the projection operator on to the subspace spanned by the eigenvectors of H_0. The perturbing operator V'_{CF} in Eq. (7) represents the crystal field potential and has the form

$$V'_{\mathrm{CF}} \equiv PV_{\mathrm{CF}}Q + QV_{\mathrm{CF}}P \tag{9}$$

with

$$V_{\mathrm{CF}} = \sum_{t,p} B^t_p \sum_i^N r^t_i C^{(t)}_p(\vartheta_i, \phi_i) \tag{10}$$

where B^t_p are the so-called crystal field parameters which describe the symmetry of the environment. Q is the orthogonal complement of P and projects on to the subspace generated by the eigenstates of all excited configurations. Thus, in accordance with Eq. (9), the perturbing operator can admix the states of all excited configurations to the states of $4\mathrm{f}^N$ configuration.

Following the standard procedure of Rayleigh–Schödinger perturbation theory, the wavefunction defined up to first order in the perturbation V'_{CF} has the form

$$\Psi_i = \Psi^0_i + \lambda \sum_{(k \neq i)}{}' \frac{\langle \Psi^0_k | V'_{\mathrm{CF}} | \Psi^0_i \rangle}{E^0_i - E^0_k} \Psi^0_k \tag{11}$$

where the zeroth-order wavefunctions are the solutions of the eigenvalue problem of H_0,

$$H_0 \Psi^0_i = E^0_i \Psi^0_i, \quad i = 1, 2, \ldots \tag{12}$$

It is common practice to assume H_0 to be a hamiltonian of the Hartree–Fock model.

The transition amplitude Γ is now determined by the terms which are of second order in the standard nomenclature of perturbation theory, namely

$$\Gamma = \lambda\{\langle \Psi^0_{\mathrm{f}} | D^{(1)}_\rho | \Psi^1_2 \rangle + \langle \Psi^1_{\mathrm{f}} | D^{(1)}_\rho | \Psi^0_{\mathrm{i}} \rangle\} + \theta(\lambda^\mu), \quad \mu \geqslant 2 \tag{13}$$

It is seen from Eq. (13) that in order to have non-zero contributions to the transition amplitude, the first-order corrections to the wavefunction have to be of opposite parity to the functions of $4\mathrm{f}^N$ configuration. This means that because of the particular form of V'_{CF} (Eq. (9)), the set of excited configurations (sum over k in Eq. (11)) is limited to those of opposite parity, i.e.

$4\mathrm{f}^{N-1}n'\ell'$ for $\ell' =$ even ($\equiv$d, g, ...)

It should be pointed out that owing to the one-particle character of all operators, only the single excitations from the 4f shell are taken into account.

Finally, the transition amplitude has the form

$$\Gamma = \sum_{Xx} \left\{ \frac{\langle \Psi^0_{\mathrm{f}} | D^{(1)}_\rho | Xx \rangle \langle Xx | QV_{\mathrm{CF}}P | \Psi^0_{\mathrm{i}} \rangle}{\Delta(E_{\mathrm{i}} - E_X)} + \frac{\langle \Psi^0_{\mathrm{f}} | PV_{\mathrm{CF}}Q | Xx \rangle \langle Xx | D^{(1)}_\rho | \Psi^0_{\mathrm{i}} \rangle}{\Delta(E_{\mathrm{f}} - E_X)} \right\} \tag{14}$$

where x denotes the states of the configuration X which is of opposite parity. Furthermore, the parity requirements for the non-vanishing matrix elements in Eq. (14) limit the crystal field potential to the odd terms only.

3.2. Standard formulation based on the length formula

In order to express the transition amplitude in terms of effective operators, one has to assume that all the states x of excited configurations are so far in energy from the ground configuration $4\mathrm{f}^N$ that the following approximations might be introduced:

(1) The states x of X are seen as degenerate.

(2) The two energy denominators of Eq. (14) are roughly the same and are approximated by the difference between the average energies of appropriate configurations.

These two approximations are discussed in the literature as the weakest point of the whole Judd–Ofelt theory. However, it should be kept in mind that owing to these approximations (even if they are becoming assumptions in some cases), the transition amplitude has a very simple and useful form. Indeed, in terms of effective tensor operators the transition amplitude is determined by the expression

$$\Gamma_{\mathrm{J-O}} = 2 \sum_{t,p}^{\mathrm{odd}} B^t_p \sum_{k,q}^{\mathrm{even}} \sum_{\ell'}^{\mathrm{even}} (-1)^q [k]^{1/2} \times \begin{pmatrix} t & 1 & k \\ p & \rho & -q \end{pmatrix} A^k_t(\ell') \langle \varrho^1(4\mathrm{f} \longrightarrow \ell') | r^t | 4\mathrm{f} \rangle \langle 4\mathrm{f}^N \Psi^0_{\mathrm{f}} | U^{(k)}_q | 4\mathrm{f}^N \Psi^0_{\mathrm{i}} \rangle \tag{15}$$

where the angular term has the form

$$A^k_t(\ell') = [k]^{1/2} \begin{Bmatrix} t & k & 1 \\ f & \ell' & f \end{Bmatrix} \langle f \| C^{(1)} \| \ell' \rangle \langle \ell' \| C^{(t)} \| f \rangle \tag{16}$$

and the radial integral contains $\varrho^1(4\mathrm{f} \rightarrow \ell')$, which is the perturbed function defined in the following way [6]:

$$\varrho^1(4\mathrm{f} \rightarrow \ell') = \sum_{n'}^{\mathrm{exc}} \frac{\langle 4\mathrm{f} | r | n'\ell' \rangle}{\Delta(4\mathrm{f}, n'\ell')} P_{n'\ell'}(r) \tag{17}$$

The perturbed function is the solution of the differential equation

$$(\epsilon_{4\mathrm{f}}-h_0^{\ell'})\varrho^1(4\mathrm{f}\longrightarrow \ell';r)=rP_{4\mathrm{f}}-\sum_{n'}^{\mathrm{occ}}P_{n'\ell'}(r)\langle n'\ell'|r|4\mathrm{f}\rangle \tag{18}$$

with

$$h_0^{\ell'}=-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2}-\frac{Z}{r}+U(r)+\frac{\ell'(\ell'+1)}{2r^2} \tag{19}$$

It should be mentioned that owing to the perturbed function approach, the radial terms of effective operators contributing to the transition amplitude contain the perturbing influence of excitations from the 4f shell to all states, discrete and continuum, of symmetry l'. This means that to perform the calculations for the complete radial basis sets, one has to solve the differential equation of Eq. (18) for a particular ℓ'.

Summarizing, it should be concluded that in the Judd–Ofelt theory the transition amplitude is determined by at most three effective operators associated with the one-particle unit tensor operators of even rank: $U^{(2)}$, $U^{(4)}$ and $U^{(6)}$.

3.3. *Alternative formulation of the $f\rightarrow f$ theory*

The difference between the transition amplitudes defined within the length and velocity formulae is equal to the matrix element of a commutator (see Eq. (4)):

$$\mathscr{T}=\langle\Psi_{\mathrm{f}}|[\vec{r},V(\vec{r},\vec{r}\,')]|\Psi_{\mathrm{i}}\rangle$$

where V is a non-local potential. Thus, in order to reach equality between the two possible formulations of one-photon f↔f transition theory, the following matrix element has to be evaluated:

$$\mathscr{T}=\langle\Psi_f^0+\lambda\Psi_f^1|PV'PD^{(1)}-D^{(1)}PV'P|\Psi_i^0+\lambda\Psi_i^1\rangle \tag{20}$$

where $D^{(1)}$ is defined by Eq. (10) and the potential V' is the Coulomb interaction operator of the form

$$V'=\sum_s\sum_{i<j}\frac{r_<^s}{r_>^{s+1}}\left(C^{(s)}(\vartheta_i\phi_i)\cdot C^{(s)}(\vartheta_j\phi_j)\right) \tag{21}$$

The first-order corrections to the wavefunctions in Eq. (20) are due to the perturbing influence of the crystal field potential V'_{CF} (Eq. (9)). The operator $V\equiv PV'P$ in Eq. (20) is a non-local operator, since the eigenfunctions of H_0 do not form the complete set and P projects on to the subspace only; actually,

$$\langle\vec{r}|V|\vec{r}\,'\rangle=\sum_j\sum_k\Psi_j^{0*}(\vec{r}\,')\Psi_k^0(\vec{r})\langle\Psi_k^0|V'|\Psi_j^0\rangle$$

In general the additional contributions to the transition amplitude are determined by two triple products of the matrix elements which differ from each other only by the order of operators:

$$\mathscr{T}=\sum_{\Psi_k^0}\sum_{Xx}\left\{\frac{\langle\Psi_{\mathrm{f}}^0|PV_{\mathrm{CF}}Q|Xx\rangle\langle Xx|D_\rho^{(1)}|\Psi_k^0\rangle\langle\Psi_k^0|PVP|\Psi_{\mathrm{i}}^0\rangle}{\Delta(E_{\mathrm{f}}-E_X)}\right.$$
$$\left.-\frac{\langle\Psi_{\mathrm{f}}^0|PVP|\Psi_k^0\rangle\langle\Psi_k^0|D_\rho^{(1)}|Xx\rangle\langle Xx|QV_{\mathrm{CF}}P|\Psi_{\mathrm{i}}^0\rangle}{\Delta(E_{\mathrm{i}}-E_X)}\right\} \tag{22}$$

Here x again denotes the states of all excited configurations X which are of opposite parity to $4\mathrm{f}^N$. Owing to the single-particle character of the operators, similarly as in the case of the standard Judd–Ofelt theory, only single excitations from the 4f shell are taken into account. In addition, it is seen that the general form of Eq. (22) could be reproduced by the product of the transition amplitude of the standard Judd–Ofelt theory (Eq. (14)) and an extra interaction between all possible states of $4\mathrm{f}^N$ configuration via the Coulomb potential operator.

Following the rules of Racah algebra and using the formalism of unit tensor operators, it is straithforward to show that the matrix element of the commutator is expressed in terms of two kinds of operators. The operators of the first kind, of one-particle origin, are within the standard parametrization scheme of the Judd–Ofelt theory and have the form

$$\Gamma_{\mathrm{nloc}}^{(1)}=\sum_s^{\mathrm{even}}(b_s-[\ell]b_0)\sum_{t,p}^{\mathrm{odd}}B_p^t\sum_{k,q}^{\mathrm{odd}}\sum_{\ell'}^{\mathrm{even}}(-1)^{k-q}$$
$$\times\begin{pmatrix}t & 1 & k\\ p & \rho & -q\end{pmatrix}A_t^k(\ell')\langle\varrho^1(4\mathrm{f}\longrightarrow\ell')|r^t|4\mathrm{f}\rangle$$
$$\langle 4\mathrm{f}^N\Psi_{\mathrm{f}}^0|U_q^{(k)}|4f^N\Psi_{\mathrm{i}}^0\rangle \tag{23}$$

where

$$b_s=R^s(4\mathrm{f}4\mathrm{f}4\mathrm{f}4\mathrm{f})\langle f\|C^{(s)}\|f\rangle^2 \tag{24}$$

and the angular part $A_t^k(\ell')$ is defined by Eq. (16), while the radial integral contains the perturbed function defined by Eq. (17). Although the tensorial form of these operators is similar to those defined within the standard Judd–Ofelt theory (Eq. (19)), the operators determining $\mathscr{T}$ are of odd rank.

In addition to the effective operators defined by Eq. (23), there are new second-order two- and three-particle objects. The two-particle effective operators of third order have been introduced into the transition theory in the model in which electron correlation effects are included. The extra contributions caused by the non-locality of the potential are determined by a general expression of the form

$$\Gamma_{\mathrm{nloc}}^{(3)}=-\sum_{s>0}^{\mathrm{even}}b_s\sum_{t,p}^{\mathrm{odd}}B_p^t\sum_{k,q}^{\mathrm{odd}}\sum_{\ell'}^{\mathrm{even}}(-1)^{k-q}$$
$$\times\begin{pmatrix}t & 1 & k\\ p & \rho & -q\end{pmatrix}A_t^k(\ell')\langle\varrho^1(4\mathrm{f}\longrightarrow\ell')|r^t|4\mathrm{f}\rangle$$
$$\langle 4\mathrm{f}^N\Psi_{\mathrm{f}}^0|[U^{(k)}\times(U^{(s)}\cdot U^{(s)})]_q^{(k)}|4\mathrm{f}^N\Psi_{\mathrm{i}}^0\rangle \tag{25}$$

The one-, two- and three-particle character of the effective operators is seen clearly when one takes into account that each unit tensor operator is an N-electron operator, i.e. $U^{(k)}=\Sigma_i u_i^{(k)}$. Furthermore, in order to collect all the one-particle operators from Eqs. (23) and (25), the coefficient b_s in Eq. (23) has to be multiplied by a factor of $-1/7$ and b_0 by 13; the remaining terms of Eq. (25) are purely two- and three-particle operators.

It is seen from Eq. (25) that again the angular and radial terms of these new effective operators are the same as in the case of the standard Judd–Ofelt approach. Furthermore, it should be pointed out that in contradiction to the standard second-order effective operators, here the rank k of all operators is odd, $k=1$, 3, 5, and the following general triangle condition should be satisfied:

$$|t-1|\leqslant k\leqslant t+1$$

where t is the rank of tensor operator of the crystal field potential defined by Eq. (10).

4. Summary

The standard Judd–Ofelt theory of one-photon f↔f transitions is based on the length form of the interaction between matter and a radiation field. It has been demonstrated in the present paper that in order to reach equivalence between the two alternative formulations of the intensity theory, the extra matrix element has to be evaluated; namely, in accordance with Eq. (4),

$$\Gamma_{\text{J–O}}=\Gamma_{\text{vel.}}+\mathcal{T} \tag{26}$$

where $\Gamma_{\text{J–O}}$ is the transition amplitude defined within the standard Judd–Ofelt theory (Eq. (15)), Γ_{vel} is its analogue based on the velocity form and $\mathcal{T}$ is the matrix element defined by Eq. (22).

The presence of the last term is caused by the non-locality of the potential of the zeroth-order hamiltonian. In the case of all approaches based on the independent particle model, the last term in Eq. (26) does not exist and the two formulations are equivalent. This particular case has been analysed by Reid [7], who assumed that the zeroth-order hamiltonian has such a form that the momentum operator is equal to the velocity operator.

The discussion of the equality between the length and velocity formulae should be completed by comments about the paper by Malta [8], who, in reformulating the transition amplitude from the length form to the velocity version, concluded that in the case of degenerate states there is an inconsistency between the two formulations. It should be kept in mind, however, that in order to compare length and velocity formulations of the f↔f transition theory, in accordance with Eq. (4), the new terms caused by the non-locality of the potential have to be taken into account. This means that if degeneracy of the initial and final states of a process is assumed, as in the standard Judd–Ofelt theory, the left-hand side of Eq. (4) vanishes, but the transition amplitude based on the velocity form does not vanish and is determined by the effective operators of Eqs. (23) and (25). Thus it is seen from the present analysis that there are two alternative formulations of the intensity theory of rare earth ions in crystals.

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