

## On the Interaction of a Radiation Field with a $nl^N$ Type Configuration

O. L. MALTA\*

*Departamento de Química da UFPE, Cidade Universitária, Recife, PE. 50000 — Brasil*

Recebido em 26/11/1980

A comparison is made between electric-dipole matrix elements within a  $nl^N$  type configuration, as given by the length and velocity formulae. Within the approximation of considering each excited configuration as a degenerate one, it is shown that up to second order the matrix elements of the momentum operator are vanishing in contrast with the Judd-Ofelt theory. This conclusion shows that it is a serious error to use the Judd-Ofelt wave functions and the velocity formula. However, up to third order, in addition to even and odd rank tensors which enter on the same footing in the matrix elements, the velocity formula predicts the contribution of two and three-particle operators which depend on the energy difference between configurations in the same way as the one-particle operators. A brief discussion of the results is made.

Uma comparação é feita entre elementos de matriz do operador momento do dipolo, atuando no interior de uma configuração do tipo  $nl^N$ , segundo as fórmulas de comprimento e velocidade. Dentro da aproximação em que se considera configurações degeneradas, é demonstrado que até segunda ordem os elementos de matriz do operador momento linear são nulos, em contraste com a teoria de Judd-Ofelt. Até terceira ordem, além de operadores unitários de ordem par e ímpar, os

---

\* Address for correspondence: Departamento de Física da UFPE, Cidade Universitária - Recife - PE - 50000 - Brasil.

quais, em termos de ordem de grandeza, contribuem igualmente para os elementos de matriz, este operador prevê a contribuição de operadores efetivos de dois e três corpos os quais apresentam a mesma dependência, sobre a diferença de energia entre configurações, que os operadores de um corpo. Os resultados são sumariamente discutidos.

## 1. INTRODUCTION

The interaction of a radiation field with the lanthanides is a subject that has received more attention after the publication of two important articles by Judd (1962) and Ofelt (1962), treating the problem of lanthanide intensities arising from electronic transitions within the  $4f^N$  configuration.

There has been many discussions in the literature (Chandrasekhar 1945, Bethe and Salpeter 1957, Fanc and Cooper 1968, Starace 1970, Grant 1974, Aharonov and Au 1979) on the most appropriate formula, length, velocity and acceleration, one should use when evaluating electric-dipole transition rates in atomic systems. The great majority of them has given attention to the length and velocity forms of the interaction hamiltonian, either concerning the evaluation of the matrix elements with approximate wavefunctions or the use of exact wavefunctions, of an approximate hamiltonian, with the inclusion of nonlocal potentials.

Judd (1962) and Ofelt (1962), in their treatment, made use of the length formula and obtained an expression for electric-dipole transition probabilities within the  $4f^N$  configuration (which becomes permitted when the atom is placed in an environment without center of inversion), in terms of a few parameters and the reduced matrix elements of the unit tensor operators  $U^k$ ). In their formula,  $\lambda$  is restricted to the values 2, 4 and 6, giving rise to the Judd-Ofelt selection rules.

In the present article, we examine this problem from the point of view of the velocity formula. To this end, second quantization methods were used in order to live technical details as transparent

as possible. The results, as expected, are shown to differ from those obtained with the length formula, the most striking point being the appearance of unit tensors  $U^{(\lambda)}$  with odd  $\lambda$  which may contribute to the intensities on the same footing as those with even  $h$ .

## 2. THE CRYSTAL FIELD AND THE POLARIZATION OF ATOMIC SYSTEMS

Electric-dipole transitions within a  $n\ell^N$  type configuration are forbidden by Laporte's rule which may, however, be violated when the atom, or ion, is found to be under the action of a crystal field.

In terms of Racah's spherical tensor operators,  $C_q^{(t)}$  (Racah 1942), we may assume that the interaction hamiltonian due to the crystal field is given by (Wybourne 1965)

$$V_{C.F.} = \sum_{t,q,j} B_q^t C_q^{(t)}(j) \quad (1)$$

where  $j$  labels the electrons outside closed shells. The coefficients  $B_q^t$  contain the radial dependence of  $V_{C.F.}$  and for our purposes we need a more precise knowledge of this dependence. Since we are directly interested in the lanthanides, it is reasonable to rewrite Eq. (1) as

$$V_{C.F.} = \sum_{t,q,j} \gamma_q^t r_j^t C_q^{(t)}(j) \quad (2)$$

where  $\gamma_q^t$  is a quantity which depends on the nature of the environment and coordination around the atomic system, and  $r_j$  the distance of the  $j$ -th electron to the origin.

The hamiltonian  $V_{C.F.}$ , has the effect of polarizing the system lowering its spherical symmetry. This effect can be taken into account (Fano and Racah 1959) by expanding a certain state, say  $|A\rangle$ , of the atomic system as a linear combination of the complete set  $|\beta \psi M_j\rangle$ , where the symbol  $\psi$  indicates that we are working in the intermediate coupling scheme and  $\beta$  stands for a unique specification of the members of the set. The coefficients in this expansion depend on  $V_{C.F.}$ .

In order to get non-vanishing electric-dipole matrix elements, the excited states  $|\beta\psi_{JM_J}\rangle$  of interest are those belonging to configurations of opposite parity to the  $n\ell^N$  one. The mixing between states is then provided by the hemiedric part of the crystal field. One approach is to use first order perturbation theory (Judd 1962) and write

$$|A\rangle = |(n\ell^N)\psi_{JM_J}\rangle + \sum_m \frac{|m\rangle\langle m| V_{C.F.} |(n\ell^N)\psi_{JM_J}\rangle}{[E(n, \ell, \psi_{JM_J}) - E(m)]} \quad (3)$$

where  $|(n\ell^N)\psi_{JM_J}\rangle$  belongs to  $n\ell^N$  and  $|m\rangle$  to a configuration that differs from  $n\ell^N$  by a single electron excitation. It has become customary (Judd 1962, Wybourne 1968, Armstrong 1971) to consider, in this expansion, the energy difference,  $E(n, \ell, \psi, J, M_J) - E(m)$ , as being approximated equal to the energy difference between the two configurations as given by the central field approximation. Thus, the quantity  $E(n, \ell, \psi, J, M_J) - E(m)$  is replaced by  $E_{n\ell} - E_{n'\ell'}$ , which depends only on the quantum numbers  $n, \ell, n'$  and  $\ell'$ . For a particular perturbing configuration, we may then write

$$|A\rangle = |(n\ell^N)\psi_{JM_J}\rangle + \frac{1}{E_{n\ell} - E_{n'\ell'}} \sum_u |u\rangle\langle u| V_{C.F.} |(n\ell^N)\psi_{JM_J}\rangle \quad (4)$$

where the complete expansion, in first order, understands a summation over  $n'\ell'$ .

The Einstein's coefficient of spontaneous emission,  $S$ , for an electric dipole transition from a state  $|A\rangle$  to a state  $|B\rangle$ , may be written, according to the length and velocity formulas, as

$$S = \frac{4e^2\omega^3}{3\hbar c^3} |\langle A | \sum_j \vec{r}_j | B \rangle|^2 \quad (5)$$

and

$$S = \frac{4e^2\omega}{3\hbar m^2 c^3} |\langle A | \sum_j \vec{p}_j | B \rangle|^2 \quad (6)$$

where  $\omega$  is the angular frequency of the transition,  $\vec{r}_j$  the position

vector of the  $j$ -th electron outside closed shells and  $\vec{P}_j$  its linear momentum.

It is well known that if  $|A\rangle$  and  $|B\rangle$  were exact eigenstates of an approximate hamiltonian for the atomic system, equations (5) and (6) would give exactly the same value of  $S$ . However, this is in general not the case, particularly in our case where  $|A\rangle$  and  $|B\rangle$  are approximated by expansions given by Eq. (4), so that we expect these equations to give different results.

### 3. MATRIX ELEMENTS

The main objective in many calculations of atomic interactions involving mixing between configurations, is to search for effective operators, acting within the ground configuration, which simulate each a mixing. To this end, tensorial techniques (Judd 1963) were proved to be extremely useful. Thus, we may cast the result given by the Judd-Ofelt theory (Judd 1962, Ofelt 1962), in terms of  $n-j$  symbols and the reduced matrix elements of  $C^{(t)}$  and the unit tensor operator  $U^{(\lambda)}$ , as

$$S = \frac{4e^2\omega^3}{3\hbar c^3} \sum_{\lambda(\text{even})} \Omega_{\lambda} \langle (n\ell^N)\psi_J || U^{(\lambda)} || (n\ell^N)\psi_{J'} \rangle^2 (2J+1)^{-1} \quad (7)$$

where

$$\Omega_{\lambda} = (2\lambda+1) \sum_{t,q} \left[ \gamma_q^t \right]^2 (2t+1)^{-1} \left| 2 \sum_{n'\ell'} \begin{pmatrix} 1 & \lambda & t \\ \ell & \ell' & \ell \end{pmatrix} \langle \ell || C^{(1)} || \ell' \rangle \times \right. \\ \left. \times \langle \ell' || C^{(t)} || \ell \rangle \langle n\ell | r^k | n'\ell' \rangle \langle n'\ell' | r^t | n\ell \rangle (E_{n\ell} - E_{n'\ell'})^{-1} \right]^2 \quad (8)$$

and  $\langle n\ell | r^k | n'\ell' \rangle$  stands for the radial integral

$$\int_0^{\infty} \phi_{n\ell} r^k \phi_{n'\ell'} r^2 dr$$

where  $\phi$  is the radial part of the one electron wave function given, in principle, by the central field approximation.

Let us now start examining what expression can be obtained for  $S$  if we consider equation (6). The procedure will then make it clear how equation (7) is obtained if we start from equation (5).

Up to second order, the leading contributions to the matrix element  $\langle A | \sum_j \tilde{P}_j | B \rangle$  may be written as

$$\frac{1}{E_{n\ell} - E_{n'\ell'}} \sum_u \langle (n\ell^N) \psi_{JM_j} | \sum_j \tilde{P}_j | u \rangle \langle u | V_{C.F.} | (n\ell^N) \psi'_{J'M_{j'}} \rangle +$$

$$+ \frac{1}{E_{n\ell} - E_{n'\ell'}} \sum_u \langle (n\ell^N) \psi_{JM_j} | V_{C.F.} | u \rangle \langle u | \sum_j \tilde{P}_j | (n\ell^N) \psi'_{J'M_{j'}} \rangle \quad (9)$$

From second quantization methods, we write the operators  $V_{C.F.}$  and  $\sum_j \tilde{P}_j$  as a sum over creation and annihilation operators which satisfy the usual Fermi-Dirac anticommutation relations. From this sum, only the operators which may connect the ground and the particular perturbing configuration, need to be considered. We may therefore extend the sum over  $u$  in (9) and include all other states of the complete set  $\{|m\rangle\}$ . Making use of the closure relation, the structure  $\sum_u |u\rangle \langle u|$  may now be removed and the two operators brought together (Judd 1967).

Two types of perturbing configurations are of interest here, these are the  $n\ell^{N-1} n'R'$  with  $R' = R \pm 1$ , configuration and  $(n'\ell')^{4\ell'+1} n\ell^{N+1}$ , with  $R' = R - 1$ , which is associated with core excitations. Let then  $a_\zeta^+$  and  $a_\zeta^-$ ,  $b_\eta$  and  $b_\eta^-$ ,  $e_\xi^+$  and  $e_\xi^-$ , annihilate and create occupied orbitals  $n\ell$ ,  $n'R'$  and  $n'\ell'$ , respectively, where greek letters stand for the pair of one electron quantum numbers  $(m_s, m_\ell)$ , the spin and orbital magnetic quantum numbers. Thus, for a particular  $n\ell^{N-1} n'R'$  perturbing configuration we may rewrite expression (9) as

$$\langle (n\ell^N) \psi_{JM_j} | \hat{O}(n'\ell') | (n\ell^N) \psi'_{J'M_{j'}} \rangle \quad (10)$$

where the operator  $\hat{O}(n'\ell')$  is given by

$$\begin{aligned} \hat{O}(n'l') &= \frac{1}{E_{nl} - E_{n'l'}} \left[ \sum_{\substack{\zeta \zeta' \\ \eta \eta'}} (a_{\zeta}^{\dagger} \langle n l \zeta | \vec{P} | n' l' \eta \rangle b_{\eta} b_{\eta'}^{\dagger} \times \right. \\ &\quad \times \langle n' l' \eta' | v_{\text{C.F.}} | n l \zeta' \rangle a_{\zeta'} + a_{\zeta}^{\dagger} \langle n l \zeta | v_{\text{C.F.}} | n' l' \eta \rangle b_{\eta} b_{\eta'} \times \\ &\quad \left. \times \langle n' l' \eta' | \vec{P} | n l \zeta' \rangle a_{\zeta'} \right] \quad (11) \end{aligned}$$

where  $v_{\text{C.F.}}$  and  $\vec{P}$  stand for the one electron operators  $\sum_{tq} \gamma_q^t r_j^t C_q^{(t)}(j)$  and  $\vec{P}_j$  respectively.

This operator may be further simplified if we use the Fermi-Dirac anticommutation relations and write

$$\begin{aligned} a_{\zeta}^{\dagger} b_{\eta} b_{\eta'}^{\dagger} a_{\zeta'} &= a_{\zeta}^{\dagger} a_{\zeta'} \delta_{\eta\eta'} - a_{\zeta}^{\dagger} b_{\eta'}^{\dagger} b_{\eta} a_{\zeta'} \\ &= a_{\zeta}^{\dagger} a_{\zeta'} \delta_{\eta\eta'} + a_{\zeta}^{\dagger} b_{\eta'}^{\dagger} a_{\zeta'} b_{\eta} \quad (12) \end{aligned}$$

Now, since  $n l^N$  has no  $n' l'$  orbitals occupied  $b_{\eta} |(n l^N) \psi^{JM}_{J'} \rangle = 0$ , and therefore we may write the operator  $O(n'l')$  as

$$\begin{aligned} \hat{O}(n'l') &= \frac{1}{E_{nl} - E_{n'l'}} \left[ \sum_{\zeta \zeta' \eta} (\langle n l \zeta | \vec{P} | n' l' \eta \rangle \langle n' l' \eta | v_{\text{C.F.}} | n l \zeta' \rangle + \right. \\ &\quad \left. + \langle n l \zeta | v_{\text{C.F.}} | n' l' \eta \rangle \langle n' l' \eta | \vec{P} | n l \zeta' \rangle) a_{\zeta}^{\dagger} a_{\zeta'} \right] \quad (13) \end{aligned}$$

For the perturbing configuration  $(n'' l'')^{4l''+1} n l^{N+1}$  we have

$$\begin{aligned} \hat{O}(n'' l'') &= \frac{1}{E_{n l} - E_{n'' l''}} \left[ \sum_{\substack{\xi \xi' \\ \xi \xi'}} (c_{\xi}^{\dagger} \langle n'' l'' \xi | \vec{P} | n l \zeta \rangle a_{\zeta} a_{\zeta'}^{\dagger} \times \right. \\ &\quad \times \langle n l \zeta' | v_{\text{C.F.}} | n'' l'' \xi' \rangle c_{\xi'} + c_{\xi}^{\dagger} \langle n'' l'' \xi | v_{\text{C.F.}} | n l \zeta \rangle a_{\zeta} a_{\zeta'}^{\dagger} \\ &\quad \left. \times \langle n l \zeta' | \vec{P} | n'' l'' \xi' \rangle c_{\xi'} \right] \quad (14) \end{aligned}$$

We use again the anticommutation relations to write

$$\begin{aligned}
 c_{\xi}^{\dagger} a_{\zeta}^{\dagger} a_{\zeta}^{\dagger} c_{\xi} &= c_{\xi}^{\dagger} (\delta_{\zeta\zeta} - a_{\zeta}^{\dagger} a_{\zeta}) c_{\xi} = \\
 &= \delta_{\xi\xi} \delta_{\zeta\zeta} - c_{\xi}^{\dagger} c_{\xi} - a_{\zeta}^{\dagger} c_{\xi}^{\dagger} a_{\xi} a_{\zeta} \\
 &= \delta_{\xi\xi} \delta_{\zeta\zeta} - c_{\xi}^{\dagger} c_{\xi} - a_{\zeta}^{\dagger} a_{\zeta} \delta_{\xi\xi} - a_{\zeta}^{\dagger} c_{\xi} a_{\zeta} c_{\xi}^{\dagger} \quad (15)
 \end{aligned}$$

and since the orbitals  $n''l''$  in  $n\ell^N$  are occupied  $c_{\zeta}^{\dagger} |(n\ell^N)\psi^{JM}_{J'}\rangle = 0$ , therefore we may write the operator  $O(n''l'')$  as

$$\begin{aligned}
 O(n''l'') &= - \frac{1}{E_{n\ell} - E_{n''l''}} \left[ \sum_{\zeta\zeta'\xi} \langle n''l''\xi | \vec{P} | n\ell\zeta \rangle \langle n\ell\zeta' | v_{\text{C.F.}} | n''l''\xi \rangle + \right. \\
 &\quad \left. + \langle n''l''\xi | v_{\text{C.F.}} | n\ell\zeta \rangle \langle n\ell\zeta' | \vec{P} | n''l''\xi \rangle a_{\zeta}^{\dagger} a_{\zeta} \right] \quad (16)
 \end{aligned}$$

In the central field approximation, the commutation relation

$$\frac{i\hbar}{m} \vec{P}_j = \vec{r}_j H_0 - H_0 \vec{r}_j \quad (17)$$

may be used, where  $H_0$  is the central field hamiltonian, to put the matrix elements of  $\vec{P}$  in the following form

$$\langle n''l''\xi | \vec{P} | n\ell\zeta \rangle = \frac{im}{\hbar} (\epsilon_{n''l''} - \epsilon_{n\ell}) \langle n''l''\xi | \vec{r} | n\ell\zeta \rangle \quad (18)$$

where  $\epsilon$  stands for single electron energies. It turns out that the energy difference in Eq. (18) must then be equal to  $E_{n\ell} - E_{n''l''}$ , as well as  $\epsilon_{n\ell} - \epsilon_{n''l''}$  must be equal to  $E_{n\ell} - E_{n''l''}$ . In this way equations (13) and (16) can be written as

$$\begin{aligned}
 \hat{O}(n'l') &= \frac{im}{\hbar} \sum_{\zeta\zeta'\eta} \langle n\ell\zeta | \vec{r} | n'l'\eta \rangle \langle n'l'\eta | v_{\text{C.F.}} | n\ell\zeta' \rangle - \\
 &\quad - \langle n\ell\zeta | v_{\text{C.F.}} | n'l'\eta \rangle \langle n'l'\eta | \vec{r} | n\ell\zeta' \rangle a_{\zeta}^{\dagger} a_{\zeta'} \quad (19)
 \end{aligned}$$

and



$$\begin{aligned} \hat{O}(n''l'') &= -\frac{im}{\hbar} \sum_{\zeta\zeta'} \left( \langle n''l''\xi | \vec{r} | n\lambda\zeta \rangle \langle n\lambda\zeta | v_{C.F.} | n''l''\xi \rangle - \right. \\ &\quad \left. - \langle n''l''\xi | v_{C.F.} | n\lambda\zeta \rangle \langle n\lambda\zeta | \vec{r} | n''l''\xi \rangle \right) a_{\zeta}^{\dagger} a_{\zeta'} \end{aligned} \quad (20)$$

where we have made in Eq. (20) the trivial replacements  $\zeta \rightarrow \zeta'$  and  $\zeta' \rightarrow \zeta$ .

Since the operators  $\hat{O}(n'l')$  and  $\hat{O}(n''l'')$  no longer depend on the energy denominators and the single electron matrix elements are vanishing for  $l' \neq l \pm 1$  and  $l'' \neq l - 1$ , we may sum over all possible values of  $n'l'$  and  $n''l''$ . Because of the minus sign in front of the right hand side of Eq. (20), we may combine the terms, in the parenthesis, from both equations (19) and (20) to form the sum over the complete set of single electron eigenstates and use closure to obtain

$$\begin{aligned} \frac{im}{\hbar} \sum_{\zeta\zeta'} \left( \langle n\lambda\zeta | \vec{r} | v_{C.F.} | n\lambda\zeta' \rangle - \langle n\lambda\zeta | v_{C.F.} | \vec{r} | n\lambda\zeta' \rangle \right) a_{\zeta}^{\dagger} a_{\zeta'} &= \\ = \frac{im}{\hbar} \sum_{\zeta\zeta'} \langle n\lambda\zeta | [\vec{r}, v_{C.F.}] | n\lambda\zeta' \rangle a_{\zeta}^{\dagger} a_{\zeta'} &= 0 \end{aligned} \quad (21)$$

since the commutator  $[\vec{r}, v_{C.F.}] = 0$ .

We have then obtained the important result that, within the approximation in which a configuration is considered to be completely degenerate, up to second order in perturbation theory the matrix elements for electric dipole transitions, according to the velocity formula, are vanishing. It must be noted that if we had started with the  $\vec{r}$  operator, instead of  $\vec{p}$ , we would have obtained non vanishing matrix elements which would in fact lead to Eq. (7).

We are then forced to go to higher order in perturbation theory. Up to second order, for the particular perturbing configurations  $n\lambda^{N-1} n'l'$  and  $n\lambda^{N-1} n''l''$ , we may expand the state  $|A\rangle$  as (once again the complete expansion understands a sum over  $n'l'$  and  $n''l''$ )

$$\begin{aligned}
|A\rangle = & (n\ell^N)\psi_{\mathcal{M}_J} + \frac{1}{E_{n\ell} - E_{n'\ell'}} \sum_u |u\rangle \langle u| V | (n\ell^N)\psi_{\mathcal{M}_J} + \\
& + \frac{1}{2} |(n\ell^N)\psi_{\mathcal{M}_J}\rangle \frac{1}{(E_{n\ell} - E_{n'\ell'})^2} \sum_u \langle (n\ell^N)\psi_{\mathcal{M}_J} | V | u\rangle \langle u | V | (n\ell^N)\psi_{\mathcal{M}_J}\rangle + \\
& + \sum_u |u\rangle \left[ \sum_x \frac{\langle u | V | x\rangle \langle x | V | (n\ell^N)\psi_{\mathcal{M}_J}\rangle}{(E_{n\ell} - E_{n'\ell'}) (E_{n\ell} - E_{n''\ell''})} - \right. \\
& \left. - \frac{\langle (n\ell^N)\psi_{\mathcal{M}_J} | V | (n\ell^N)\psi_{\mathcal{M}_J}\rangle \langle u | V | (n\ell^N)\psi_{\mathcal{M}_J}\rangle}{(E_{n\ell} - E_{n'\ell'})} \right] \quad (22)
\end{aligned}$$

where  $|x\rangle$  belongs to  $n\ell^{N-1}n''\ell''$ , and

$$V = -U + V_C + V_{S.O.} + V_{C.F.}$$

where  $U, V_C, V_{S.O.}$  represent the central field, the coulombic, the spin-orbit and the crystal field potential energies respectively. Let

$$\hbar = V_C - U$$

then the leading contribution, up to third order, to the electric dipole matrix element is given by

$$\begin{aligned}
\sum_u \langle (n\ell^N)\psi_{\mathcal{M}_J} | \sum_j \vec{P}_j | u\rangle & \left[ \sum_x \frac{\langle u | \hbar | x\rangle \langle x | V_{C.F.} | (n\ell^N)\psi^{JM_{J_1}}\rangle}{(E_{n\ell} - E_{n'\ell'}) (E_{n\ell} - E_{n''\ell''})} - \right. \\
& - \frac{\hbar \langle \psi^i | \langle u | V_{C.F.} | (n\ell^N)\psi^{JM_{J_1}}\rangle}{(E_{n\ell} - E_{n'\ell'})} + \sum_u \left[ \sum_x \right. \\
& \left. \frac{\langle (n\ell^N)\psi_{\mathcal{M}_J} | V_{C.F.} | x\rangle \langle x | \hbar | u\rangle}{(E_{n\ell} - E_{n'\ell'}) (E_{n\ell} - E_{n''\ell''})} - \frac{\hbar \langle \psi \rangle \langle (n\ell^N)\psi_{\mathcal{M}_J} | V_{C.F.} | u\rangle}{(E_{n\ell} - E_{n'\ell'})^2} \right] \times \\
& \times \langle u | \sum_j \vec{P}_j | (n\ell^N)\psi^{JM_{J_1}}\rangle \quad (23)
\end{aligned}$$

where

$$\hbar(\psi) = \langle (n\ell)^N \psi_{JM} | \hbar | (n\ell)^N \psi_{JM} \rangle \quad (24a)$$

and

$$\hbar(\psi') = \langle (n\ell)^N \psi'_{J'M_{J'}} | \hbar | (n\ell)^N \psi'_{J'M_{J'}} \rangle \quad (24b)$$

Let us first work out the terms in expression (23) containing  $\hbar(\psi)$  and  $\hbar(\psi')$ . It can be easily seen that an effective contribution is obtained which may be expressed through the operator

$$\begin{aligned} \hat{O}_1(n'\ell') = & \frac{-im}{\hbar(E_{n\ell} - E_{n'\ell'})} \sum_{\zeta\zeta'\eta} \left[ \hbar(\psi') \langle n\ell\zeta | \vec{r} | n'\ell'\eta \rangle \langle n'\ell'\eta | v_{C.F.} | n\ell\zeta' \rangle - \right. \\ & \left. - \hbar(\psi) \langle n\ell\zeta | v_{C.F.} | n'\ell'\eta \rangle \langle n'\ell'\eta | \vec{r} | n\ell\zeta' \rangle \right] a_{\zeta'}^{\dagger} a_{\zeta} \end{aligned} \quad (25)$$

We may now use the identities.

$$\hbar(\psi') = \frac{1}{2} \left[ \hbar(\psi') + \hbar(\psi) \right] + \frac{1}{2} \left[ \hbar(\psi') - \hbar(\psi) \right] \quad (26a)$$

and

$$\hbar(\psi) = \frac{1}{2} \left[ \hbar(\psi') + \hbar(\psi) \right] - \frac{1}{2} \left[ \hbar(\psi') - \hbar(\psi) \right] \quad (26b)$$

to write Eq. (25) in the form

$$\begin{aligned} \hat{O}_1(n'\ell') = & \frac{-im[\hbar(\psi') + \hbar(\psi)]}{2\hbar(E_{n\ell} - E_{n'\ell'})} \sum_{\zeta\zeta'\eta} \left( \langle n\ell\zeta | \vec{r} | n'\ell'\eta \rangle \langle n'\ell'\eta | v_{C.V.} | n\ell\zeta' \rangle - \right. \\ & \left. - \langle n\ell\zeta | v_{C.F.} | n'\ell'\eta \rangle \langle n'\ell'\eta | \vec{r} | n\ell\zeta' \rangle \right) a_{\zeta'}^{\dagger} a_{\zeta} - \\ & - \frac{im\omega}{2(E_{n\ell} - E_{n'\ell'})} \sum_{\zeta\zeta'\eta} \left( \langle n\ell\zeta | \vec{r} | n'\ell'\eta \rangle \langle n'\ell'\eta | v_{C.F.} | n\ell\zeta' \rangle \right. \\ & \left. + \langle n\ell\zeta | v_{C.F.} | n'\ell'\eta \rangle \langle n'\ell'\eta | \vec{r} | n\ell\zeta' \rangle \right) a_{\zeta'}^{\dagger} a_{\zeta} \end{aligned} \quad (27)$$

where we have used the fact that

$$h(\psi') - h(\psi) = \hbar\omega$$

As we have done before, after using the second quantized forms for the operators  $\sum_j \vec{P}_j$ ,  $h$  and  $V_{C.F.}$  and then removing the structures  $\sum_u |u\rangle\langle u|$  and  $\sum_x |x\rangle\langle x|$ , we readily obtain from the remaining terms in (23) the following contributions for  $n''l'' = n'l'$ :

$$\begin{aligned} & \text{The one-particle operator involving the central potential } U = \\ & = \sum_j u_j(r) \\ & - \frac{im}{\hbar(E_{nl} - E_{n'l'})} [(N-1)\langle nl|u(r)|nl\rangle + \langle n'l'|u(r)|n'l'\rangle] \times \\ & \times \sum_{\zeta\zeta'\eta} (\langle nl\zeta|\vec{r}|n'l'\eta\rangle\langle n'l'\eta|v_{C.F.}|nl\zeta'\rangle - \\ & - \langle nl\zeta|v_{C.F.}|n'l'\eta\rangle\langle n'l'\eta|\vec{r}|nl\zeta'\rangle) \times a_{\zeta}^{\dagger}a_{\zeta'}, \end{aligned} \quad (28)$$

$$\begin{aligned} & \text{The two-particle operator involving the coulombic potential } V_C = \\ & = \sum_{i>j} v_{ij} \\ & - \frac{im}{\hbar(E_{nl} - E_{n'l'})} \sum_{\substack{\zeta\zeta'\xi\xi' \\ \eta\eta'}} (\langle nl\zeta|\vec{r}|n'l'\eta\rangle\langle nl\xi n'l'\eta|v_{12}|n'l'\eta nl\xi'\rangle \times \\ & \times \langle n'l'\eta|v_{C.F.}|nl\zeta'\rangle - \langle nl\zeta|v_{C.F.}|n'l'\eta\rangle\langle nl\xi n'l'\eta|v_{12}|n'l'\eta nl\xi'\rangle \times \\ & \times \langle n'l'\eta|\vec{r}|nl\zeta'\rangle) a_{\zeta}^{\dagger}a_{\xi}^{\dagger}a_{\xi}a_{\zeta'}, \end{aligned} \quad (29)$$

and

$$\frac{im}{\hbar(E_{nl} - E_{n'l'})} \sum_{\substack{\zeta\zeta'\xi\xi' \\ \eta\eta'}} (\langle nl\zeta|\vec{r}|n'l'\eta\rangle\langle nl\xi n'l'\eta|v_{12}|nl\xi' n'l'\eta'\rangle \times$$

$$\begin{aligned} & \times \langle n'l'\eta' | v_{C.F.} | n\ell\zeta' \rangle - \langle n\ell\zeta | v_{C.F.} | n'l'\eta' \rangle \langle n\ell\xi n'l'\eta' | v_{12} | n\ell\xi' n'l'\eta' \rangle \times \\ & \times \langle n'l'\eta | \vec{r} | n\ell\zeta' \rangle a_{\zeta}^{\dagger} a_{\xi}^{\dagger} a_{\xi'} a_{\zeta'} \end{aligned} \quad (30)$$

and the three-particle operator

$$\begin{aligned} & \frac{im}{2\hbar(E_{n\ell} - E_{n'l'})} \sum_{\substack{\zeta\zeta'\xi\xi' \\ \eta\eta'v}} \left[ \langle n\ell\zeta | \vec{r} | n'l'v \rangle \langle n'l'v | v_{C.F.} | n\ell\zeta' \rangle - \right. \\ & \left. - \langle n\ell\zeta | v_{C.F.} | n'l'v \rangle \langle n'l'v | \vec{r} | n\ell\zeta' \rangle \right] \langle n\ell\xi n\ell\eta | v_{12} | n\ell\eta' n\ell\xi' \rangle \times \\ & \times a_{\zeta}^{\dagger} a_{\xi}^{\dagger} a_{\eta}^{\dagger} a_{\xi'} a_{\eta'} a_{\zeta'} \end{aligned} \quad (31)$$

The operator (28) may be combined with  $\hat{O}_1(n'l')$  in Eq. (27) to give

$$\begin{aligned} \hat{O}_2(n'l') &= \frac{-im}{\hbar(E_{n\ell} - E_{n'l'})} \left[ \langle n'l' | u(x) | n'l' \rangle - \langle n\ell | u(x) | n\ell \rangle + \frac{1}{2} V_C(\psi') + \right. \\ & \left. + \frac{1}{2} V_C(\psi) \right] \sum_{\zeta\zeta'\eta} \left( \langle n\ell\zeta | \vec{r} | n'l'\eta \rangle \langle n'l'\eta | v_{C.F.} | n\ell\zeta' \rangle - \right. \\ & \left. - \langle n\ell\zeta | v_{C.F.} | n'l'\eta \rangle \langle n'l'\eta | \vec{r} | n\ell\zeta' \rangle \right) a_{\zeta}^{\dagger} a_{\zeta'} - \\ & - \frac{im}{2(E_{n\ell} - E_{n'l'})} \sum_{\zeta\zeta'\eta} \left( \langle n\ell\zeta | \vec{r} | n'l'\eta \rangle \langle n'l'\eta | v_{C.F.} | n\ell\zeta' \rangle + \right. \\ & \left. + \langle n\ell\zeta | v_{C.F.} | n'l'\eta \rangle \langle n'l'\eta | \vec{r} | n\ell\zeta' \rangle \right) a_{\zeta}^{\dagger} a_{\zeta'} \end{aligned} \quad (32)$$

where we have used the fact that

$$\hbar(\psi') = V_C(\psi') - N \langle n\ell | u(x) | n\ell \rangle$$

and

$$h(\psi) = V_C(\psi) - N \langle n\ell | u(r) | n\ell \rangle$$

There is no apparent way in which the operators (29), (30) and (31) are able to cancel some of the terms in Eq. (32). Thus, in order to compare the results obtained from the valocity formula with the Judd-Ofelt theory (Judd 1962, Ofelt 1962), we should be primarily interested in Eq. (32) which involves one-particle operators.

Since the operators in this equation do not act on the spin space, the greek letters may stand for the one electron orbital magnetic quantum number. We now use the expansion

$$\vec{r} = r \sum_{q'} (-1)^{q'} C_{q'}^{(1)} \vec{e}_{-q'} \quad (33)$$

where  $\vec{e}_{-q'}$  is a unit spherical vector (Edmonds 1957), and use the Wigner Eckart theorem to obtain an expression depending on the structures

$$(-1)^{\ell-\zeta+\ell'-\eta} \begin{Bmatrix} \ell & 1 & \ell' \\ -\zeta & q' & \eta \end{Bmatrix} \begin{Bmatrix} \ell' & 1 & \ell \\ -\eta & q & \zeta' \end{Bmatrix} \pm (-1)^{\ell-\zeta+\ell'-\eta} \begin{Bmatrix} \ell & 1 & \ell' \\ -\zeta & q & \eta \end{Bmatrix} \begin{Bmatrix} \ell' & 1 & \ell \\ \eta & q' & \zeta' \end{Bmatrix} \quad (34)$$

where the minus and plus signs refer to the first and second sum on the right hand side of Eq. (32) respectively. The equation

$$\sum_{m_3} (-1)^{\ell_1+\ell_2+\mu_1+\mu_2} \begin{Bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{Bmatrix} \begin{Bmatrix} \ell_1 & \ell_2 & j_3 \\ \mu_1 & -\mu_2 & m_3 \end{Bmatrix} \\ = \sum_{\lambda Q} (-1)^{\lambda+Q} (2\lambda+1) \begin{Bmatrix} j_1 & j_2 & j_3 \\ \ell_1 & \ell_2 & \lambda \end{Bmatrix} \begin{Bmatrix} \ell_1 & j_2 & \lambda \\ -\mu_1 & m_1 & Q \end{Bmatrix} \begin{Bmatrix} j_1 & \ell_2 & \lambda \\ m_1 & \mu_2 & -Q \end{Bmatrix} \quad (35)$$

may then be used, and it is immediately seen that the structure (34) with the minus sign will involve only odd values of  $\lambda$  (Eq. (35)), while the structure with the plus sign will involve only even values of  $\lambda$ . After that, it is a simple matter to rearrange the whole expression and sum over the indices  $\zeta$  and  $\zeta'$  to obtain the coupled operator (Judd 1967)

$$(\underline{a}^\dagger \underline{a})_0^{(0\lambda)}_Q$$

which is the second-quantized form of

$$-W^{(0\lambda)}_0 Q$$

where (Judd 1963)

$$W_0^{(0\lambda)}_Q = \left[ \frac{(2\lambda+1)}{2} \right]^{1/2} U_Q^{(\lambda)}$$

We finally obtain for  $\hat{O}_2(n'l')$  the expression

$$\begin{aligned} \hat{O}_2(n'l') &= \frac{-im}{\hbar(E_{n\lambda} - E_{n'l'})} I(\psi, \psi', n\lambda, n'l') \sum_{tqq'} \langle n\lambda | r | n'l' \rangle \langle n'l' | r^t | n\lambda \rangle \times \\ &\times \langle \ell || C^{(1)} || \ell' \rangle \langle \ell' || C^{(t)} || \ell \rangle \gamma_q^t 2 \sum_{\lambda Q}^{\text{odd}} (-1)^{Q+q'} (2\lambda+1) \left\{ \begin{matrix} 1 & \ell & \ell \\ \ell & t & \lambda \end{matrix} \right\} \left\{ \begin{matrix} 1 & t & \lambda \\ q' & q & -Q \end{matrix} \right\} \times \\ &\times U_Q^{(\lambda)} e^{-q'} + \frac{im \omega}{(E_{n\lambda} - E_{n'l'})} \sum_{tqq'} \langle n\lambda | r | n'l' \rangle \langle n'l' | r^t | n\lambda \rangle \\ &\times \langle \ell || C^{(1)} || \ell' \rangle \langle \ell' || C^{(t)} || \ell \rangle \gamma_q^t \sum_{\lambda Q}^{\text{even}} (-1)^{Q+q'} (2\lambda+1) \times \\ &\left\{ \begin{matrix} 1 & \ell & \ell' \\ \ell & t & \lambda \end{matrix} \right\} \left\{ \begin{matrix} 1 & t & \lambda \\ q' & q & -Q \end{matrix} \right\} U_Q^{(\lambda)} e^{-q'} \end{aligned} \quad (36)$$

where

$$I(\psi, \psi', n\lambda, n'l') = [\langle n'l' | u(r) | n'l' \rangle - \langle n\lambda | u(r) | n\lambda \rangle + \frac{1}{2} V_C(\psi) + \frac{1}{2} V_C(\psi')] \quad (37)$$

The term in Eq. (36) involving the even rank tensors  $\underline{U}^{(\lambda)}$ , if multiplied by two, corresponds to the same effective operator as found

by Judd (1962) and Ofelt (1962). Thus, at least the contribution from one-particle operators, because of the factor 2 and the term involving odd rank tensors in Eq. (36), differs qualitatively and quantitatively according to which of the formula, length or velocity, is used.

#### 4. DISCUSSION AND CONCLUDING REMARKS

If an equivalent thermal population, of the Stark components of the initial level, is assumed, we may sum over  $M_{J'}$ , and average over  $M_J$  to obtain from Eqs. (6) and (36) the following expression for S,

$$S = \frac{4}{3} \frac{e^3 \omega}{\hbar^2 c^3} I^2 (\psi, \psi', n\ell, n'\ell') \sum_{\lambda}^{\text{odd}} T_{\lambda} \langle (n\ell^N) \psi_J || U^{(\lambda)} || (n\ell^N) \psi'_{J'} \rangle^2 \times \\ \times (2J+1)^{-1} + \frac{4}{3} \frac{e^2 \omega^3}{\hbar c^3} \sum_{\lambda}^{\text{even}} \Omega_{\lambda} \langle (n\ell^N) \psi_J || U^{(\lambda)} || (n\ell^N) \psi'_{J'} \rangle^2 (2J+1)^{-1} \quad (38)$$

where

$$T_{\lambda} = \sum_q |\gamma_q^{\lambda}|^2 \left[ \langle n\ell | r | n'\ell' \rangle \langle n'\ell' | r^{\lambda} | n\ell \rangle \langle \ell || C^{(\lambda)} || \ell' \rangle \times \right. \\ \left. \times \langle \ell' || C^{(\lambda)} || \ell \rangle \begin{Bmatrix} 1 & \ell & \ell' \\ \ell & \lambda & \lambda \end{Bmatrix} \frac{2}{(E_{n\ell} - E_{n'\ell'})} \right]^2 \quad (39)$$

and

$$\Omega_{\lambda} = (2\lambda+1) \sum_{tq} \frac{|\gamma_q^t|^2}{(2t+1)} \left[ \langle n\ell | r | n'\ell' \rangle \langle n'\ell' | r^t | n\ell \rangle \langle \ell || C^{(1)} || \ell' \rangle \times \right. \\ \left. \times \langle \ell' || C^{(t)} || \ell \rangle \begin{Bmatrix} 1 & \ell & \ell' \\ \ell & t & \lambda \end{Bmatrix} \frac{1}{(E_{n\ell} - E_{n'\ell'})} \right]^2 \quad (40)$$

In Eq. (38), we have used the fact that since  $h$  is odd, the only, non-vanishing 6- $j$  symbols in this equation are those for which  $t=\lambda$ .



The complete expression, up to third order, for  $S$  would of course include not only a summation over  $n'l'$ , but also core excitations and those terms in (23) for which  $n''l'' \neq n'l'$ . However, it is likely that (28), (29), (30) and (31), if a sum over  $n'l'$  is taken, given the most important contributions. These contributions could also be obtained from the second order treatment provided the energy denominators were corrected, to first order, by the inclusion of the appropriate matrix elements of  $h = V_C - U$ .

The real problem raised in the present analysis is a rather delicate one, that is the basic reasons for the differences, as we have theoretically shown, obtained when Eqs. (5) and (6) are used in the intensity problem of transitions within a configuration, where the states are approximated by Eq. (4). No arguments concerning the region, near, intermediate or far from the nucleus, where the radial part of the states is more accurate could be used here since in the present approach a conversion from  $\vec{P}$  to  $\vec{r}$  single-electron matrix elements is possible.

A detailed analysis of this problem, and of the precise form of the contributions from the two and three-particles operators (29), (30) and (31), is the subject of a next article.

I am deeply grateful to Professor B. R. Judd for helpful discussions and interest on this work, to Professor G. F. de Sá for constant help, to Maria da Silva for technical help, and FINEP and the Departamento de Física da UFPE for financial support and accommodations.

## REFERENCES

- Aharonov Y. and Au C.K., 1979, Phys. Rev. A, 20, 1553.  
 Armstrong L. Jr., 1971, *Theory of the Hyperfine Structure of Free Atoms* (Wiley, Interscience, N. York).  
 Bethe H.A. and Salpeter E.E., 1957, *Quantum Mechanics of one-and two - Electron Atoms* (Berlin, Springer).  
 Chandrasekhar S., 1945, Astrophys. J., 102, 223.

- Edmonds A. R. , 1957, *Angular Momentum in Quantum Mechanics* ( Princeton University Press, New Jersey).
- Fano U. and Cooper J.W., 1968, *Rev. Mod. Phys.* 40, 441.
- Fano U. and Racah G., 1959, *Irreducible Tensorial Sets* (Academic Press Inc., N. York).
- Grant I.P., 1974, *J.Phys. B: Atom. Molec. Phys.*, 7, 1458.
- Judd B.R., 1962, *Phys. Rev.*, 127, 750.
- Judd B.R. , 1963, *Operator Techniques in Atomic Spectroscopy* (Mc Graw-Hill Book Company, N.York).
- Judd B.R. , 1967, *Second Quantization and Atomic Spectroscopy* (Johns Hopkins Press, Baltimore, Maryland).
- Ofelt G.S., 1962, *J.Chem.Phys.*, 37, 511.
- Racah G., 1942, *Phys. Rev.*, 62, 438
- Wybourne B.G., 1965, *Spectroscopic Properties of Rare Earths* (John Wiley and Sons, N.York).
- Wybourne B.G., 1968, *J.Chem.Phys.*, 25, 2596.