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MULTIPHOTON EXCITATIONS IN VIBRATIONAL - ROTATIONAL STATES OF DIATOMIC MOLECULES IN INTENSE ELECTROMAGNETIC FIELD

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ABSTRACT

We present a theory and outline a calculational procedure for evaluating transition amplitudes of multiphoton excitations of vibrational-rotational levels in diatomic molecules. This theory can be utilized in studying behavior of molecules in intense electromagnetic fields.

Behaviour of atoms and molecules in intense electromagnetic fields are currently being investigated with much interest.[1] Recently Reiss[2] has proposed a non-perturbative method for treatment of multi-photon transitions in atoms. We propose an analogous theory for transitions between vibrational-rotational levels in diatomic molecules and give a calculational procedure for making specific predictions regarding such transitions. This would throw light on the currect laboratory experiments with intense field in the microwave region as well as on molecular phenomena in astrophysics involving intense radiation.

The Hamiltonian of a diatomic molecule in an electromagnetic field can be written as

$$H = H_0 + H'$$

where the molecular Hamiltonian

$$H_0 = \sum \frac{1}{2m_i} \vec{p}_i^{\,2} + \sum \frac{1}{2M_j} \vec{P}_j^{\,2} + V(\vec{r}_1, \vec{r}_2 \cdots \vec{r}_N ; R_1, R_2)$$

and the interaction

$$H' = -\sum \frac{e}{m_i} \vec{A}_i \cdot \vec{p}_i + \sum \frac{e}{M_j} Z_j \vec{A}_j \cdot \vec{P}_j$$

$$+ \sum \frac{1}{2m_i} (e\vec{A}_i)^2 + \sum_j \frac{1}{2M_j} (eZ_j \cdot A_j)^2$$

$V(\vec{r}_1 \cdots \vec{r}_n ; \vec{R}_1, \vec{R}_2)$ is the electrostatic potential of the molecule, $\vec{A}_i = a(\vec{X}_i)\hat{\epsilon} \cos\omega t$ is the vector potential at the position, $\vec{X}_i$, of the i^{th} particle, Z_j is the charge on the j^{th} nucleus, $\vec{\nabla} \cdot \vec{A}_i = 0$ (Coulomb gauge). $a(\vec{X}_i)$ is the field strength, $\hat{\epsilon}$ and ω are the polarization direction and the frequency, respectively. $\vec{r}_i$ signify the postions of the electrons and $\vec{R}_j$ that of the nuclei.

In the large wave length approximation[3] a solution of the full

Schrodinger equation

$$H \Psi_\alpha = i \frac{\partial}{\partial t} \Psi_\alpha$$

can be written as [2]

$$\Psi_\alpha = e^{i \sum e \vec{A}(t) \cdot \vec{r}_i + \sum e Z_j \cdot \vec{A}(t) \cdot \vec{R}_j} \cdot \Phi_\alpha \,, \qquad (1)$$

$$\omega / E_{if} \ll 1 \,, \quad e a a_0 \omega / E_{if} \ll 1 \,.$$

where

$$H_0 \Phi_\alpha = i \frac{\partial}{\partial t} \Phi_\alpha$$

In the above $\vec{A}(t) = a \hat{\epsilon} \cos\omega t$, a = a(0), and N is the total number of electrons.

Assuming Born-Oppenheimer approximation for the molecule [4], we write

$$\Phi_\alpha = \chi_\vartheta(R) \left(\frac{2j+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^{(j)*}_{mk}(\hat{R}) \, \psi_e(\vec{r}_1, \cdots \vec{r}_N / R) \, e^{iE_\alpha t} \qquad (2)$$

where $R = |\vec{R}_1 - \vec{R}_2|$.

Confining presently to excitations between vibrational-rotational levels for the ground electronic state, the transition matrix for $|i> \to |f>$, can be written as

$$T_{fi} = i(E_f - E_i) \int_{-\infty}^{\infty} dt \; \langle \Phi_f | \, Exp\{ie(\sum \vec{A}(t) \cdot \vec{r}_i + \sum Z_j \vec{A}(t) \cdot \vec{R}_j)| \Phi_i \rangle \qquad (3a)$$

where $(E_f - E_i)$ is the energy difference between the initial and the final states. (For excitations of levels of different electronic states we only need to set the initial and final states ψ_e's to be different; the rest of the analysis would remain unaffected.) On chosing the center of mass as the origin the exponential in Eq. (3a) becomes

$$Exp\left(ie\left\{\sum \vec{A}(t)\cdot\vec{r}_i + \beta\,\vec{A}(t)\cdot\vec{R}\right\}\right)$$

where $$\beta = (z_1 M_2 - z_2 M_1)/(M_1 + M_2) \quad .$$

To simplify the integration over t in Eq. (3a) and also to get a better insight into the transition process it is convenient to expand the exponentials above in Bessel functions. We then find

$$\bar{c}_{fi} = 2\pi\, i^{n+2}(E_f - E_i)\,\delta(E_f - E_i - n\omega + \omega')\,\bar{T}_{fi}^{(n,1)} \tag{3b}$$

where

$$\bar{T}_{fi}^{(n,1)} = \langle \chi_{\omega_f}(R)\left(\frac{2j_f+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^{*(j_f)}_{m_f K_f}(\hat{R})\,\psi_e(\vec{r}_1,\cdots\vec{r}_N/R)\,/$$

$$J_n\left(e\sum \vec{r}_i\cdot\vec{a} + e\beta\,\vec{R}\cdot\vec{a}\right)\,J_1\left(e\sum \vec{r}_i\cdot\vec{a}' + e\beta\,\vec{R}\cdot\vec{a}'\right)/$$

$$\psi_e(\vec{r}_1,\cdots\vec{r}_N/R)\left(\frac{2j_i+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^{*(j_i)}_{m_i K_i}(\hat{R})\,\chi_{\omega_i}(R)\rangle \tag{3c}$$

The delta function in Eq. (3b) shows, of course, that the transition does not occur unless the energy difference is bridged by the impinging photon energy. For a monochromatic beam of low energy photons of frequency ω (with which we are concerned here) this can be achieved, in genegal, by a multi-photon process where n-photons simultaneously give up energy to the target and any excess of energy is released as a weak photon ω', subsequently[5].

We now proceed to outline a systematic method for evaluating $T_{fi}^{(n,1)}$. Considerable simplification is achieved if the nuclear coordinates in the transition matrix could be separated out as a factor from the electronic

part. To this effect we use an addition theorem[6] of Bessel function in Eq. (3c) and rewrite the T-matrix as follows

$$\langle \chi_{v_f}(R) \Big| \sum_{p_0 \gamma_0 = -\infty}^{+\infty} N_{p_0\gamma_0}(R)\; M_{p_0\gamma_0}(R) \Big| \chi_{v_i}(R) \rangle = T_{fi}^{(n,l)} \qquad (4a)$$

where

$$N_{p_0\gamma_0}(R) = \left\langle \left(\frac{2j_f+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^{(j_f)*}_{m_f K_f}(\hat{R}) \Big| \; J_{n-p_0}(e\beta \vec{R}\cdot\vec{a}) \, J_{l-\gamma_0}(e\beta \vec{R}\cdot\vec{a}') \Big| \mathcal{D}^{(j_i)}_{m_i K_i}(\hat{R}) \left(\frac{2j_i+1}{8\pi^2}\right)^{\frac{1}{2}} \right\rangle \qquad (4b)$$

and

$$M_{p_0\gamma_0}(R) = \left\langle \Psi_e(\vec{r}_1, \cdots \vec{r}_N / R) \Big| J_{p_0}\left(e \sum_i \vec{r}_i \cdot \vec{a}\right) J_{\gamma_0}\left(e \sum \vec{r}_i \cdot \vec{a}'\right) \Big| \Psi_e(\vec{r}_1 \cdots \vec{r}_N / R) \right\rangle . \qquad (4c)$$

To evaluate $N_{p_0\gamma_0}$ we now use the well-known integral representation[7] of Bessel function and obtain

$$N_{p_0\gamma_0} = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} e^{-i(n-p_0)\theta} d\theta \int_{-\pi}^{\pi} e^{-i(l-\gamma_0)\theta'} d\theta' \left\langle \mathcal{D}^{(j_f)*}_{m_f K_f} \Big| Exp\{ i\beta\vec{R}\cdot\vec{a} \sin\theta + i\beta \vec{R}\cdot\vec{a}' \sin\theta' \} \Big| \mathcal{D}^{(j_i)*}_{m_i K_i} \right\rangle \cdot \{(2j_f+1)(2j_i+1)\}^{\frac{1}{2}} / (8\pi^2) \qquad (5a)$$

Expanding the exponentials in terms of Spherical Bessel functions we get

$$N_{p_0\gamma_0} = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} e^{-i(n-p_0)\theta} d\theta \int_{-\pi}^{\pi} e^{-i(l-\gamma_0)\theta'} d\theta' \left\langle \left(\frac{2j_f+1}{8\pi^2}\right)^{\frac{1}{2}} \mathcal{D}^{(j_f)*}_{m_f K_f}(\hat{R}) / (4\pi)^2 \right.$$
$$\sum_{lm} j_l(\delta\beta R)\, Y_{lm}(\hat{R})\, Y^*_{lm}(\hat{\epsilon}) \sum_{l'm'} j_{l'}(\delta'\beta R)\, Y^*_{l'm'}(\hat{R})\, Y_{l'm'}(\hat{\epsilon}') \Big|$$
$$\left. \mathcal{D}^{(j_i)*}_{m_i K_i}(\hat{R}) \left(\frac{2j_i+1}{8\pi^2}\right)^{\frac{1}{2}} \right\rangle \qquad (5b)$$

where $\delta = ea\sin\theta$, $\delta' = ea'\sin\theta'$.

The integration over the rotation angles $\hat{R}$ can be performed at once; the result is

$$\left\langle \left(\frac{2j_f+1}{8\pi^2}\right) \mathcal{D}^{(j_f)*}_{m_f K_f}(\hat{R}) \middle| Y_{\ell m}(\hat{k})\, Y_{\ell' m'}(\hat{R}) \middle| \mathcal{D}^{(j_i)*}_{m_i K_i}(\hat{R}) \left(\frac{2j_i+1}{8\pi^2}\right)^{\frac{1}{2}} \right\rangle$$

$$= \frac{1}{4\pi} \{(2j_f+1)(2j_i+1)(2\ell+1)(2\ell'+1)\}^{\frac{1}{2}} \sum_{LM} (-1)^{-M+m_f-K_f} (2L+1)$$

$$\begin{pmatrix} \ell & \ell' & L \\ m & m' & M \end{pmatrix} \begin{pmatrix} \ell & \ell' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f & L & j_i \\ m_f & M & m_i \end{pmatrix} \begin{pmatrix} j_f & L & j_i \\ -K_f & 0 & K_i \end{pmatrix}$$

$$\equiv B^{j_f j_i K_f \ell \ell'}_{m_f m_i K_i m m'} \tag{6}$$

The θ and θ' integrations are of a different kind. Let the integration over θ be

$$\mathcal{F}_p(\ell, b) = \int_{-\pi}^{\pi} e^{-ip\theta} J_\ell(b \sin\theta)\, d\theta \tag{7a}$$

To carry it out we first replace the Spherical Bessel functions by the integral representation involving Legendre Polynomials[8] $P_\ell(X)$ where $X = \cos\theta$, and obtain

$$\mathcal{F}_p(\ell, b) = \pi(-1)^\ell [1 + (-1)^{p+\ell}] \int_0^1 J_p(bx) P_\ell(x)\, dx \tag{7b}$$

The integration over x can now be performed explicitly[9] giving

$$\mathcal{F}_p(\ell, b) = \pi(-1)^\ell [1 + (-1)^{p+\ell}] \sum_{k=0}^{\ell} C_{k\cdot} (b)^{-k-1} [(p+k-1)$$

$$b\,J_p(b) + S_{k-1,\,p-1}(b) - b\,J_{p-1}(b)\,S_{k,p}(b)$$

$$+\ 2^k\,\Gamma\left(\tfrac{1}{2}+\tfrac{1}{2}k+\tfrac{1}{2}p\right)\Big/\Gamma\left(\tfrac{1}{2}+\tfrac{1}{2}p-\tfrac{1}{2}k\right) \qquad (7c)$$

where $b = ea\beta R$

C_k are known constants in $P_\ell(x) = \sum_{k=0}^{\ell} C_k\,x^k$,

and $S_{k,p}(b)$ are Lommel functions[10].

The integration over θ' can be performed in exactly the same way. Combining Eqs. (5), (6) and (7) we obtain

$$N_{p_0 q_0} = 4 \sum \Xi_{n-p_0}(\ell, b)\,\Xi_{l-q_0}(\ell', b')\,B^{j_f j_i k_f \ell\ell'}_{m_f m_i k_i mm'}\,Y^{*}_{\ell m}(\hat{\epsilon})\,Y_{\ell' m'}(\hat{\epsilon}') \qquad (8)$$

The spherical harmonics appearing in Eq. (8) determine the directions of polarizations of the incident and emitted photons.

The matrix elements $M_{p_0 q_0}$ for the electronic coordinates can be simplified much in the same way as above. Thus writing the electronic wave functions ψ_e as a product of single center molecular orbitals of the form[11]

$$\phi_{j}(\vec{r}/R) = \sum_{\lambda\mu_j} \frac{1}{r}\,U_\lambda(r/R)\,Y_{\lambda\mu_j}(\hat{r})$$

the contribution from each electron can be reduced to the form of Eq. (8). We get the result[12]

$$M_{p_{j-1}-p_j,\,q_{j-1}-q_j} = 4 \sum_{\ell m \ell' m' \lambda\lambda'\mu_j} \left\langle U_\lambda(r/R) \middle| \Xi_{p_{j-1}-p_j}(\ell, ear)\,\Xi_{q_{j-1}-q_j}(\ell', ea'r) \middle| U_{\lambda'}(r/R) \right\rangle B^{\lambda\lambda' o \ell\ell'}_{\mu_j \mu_j o mm'}\,Y^{*}_{\ell m}(\hat{\epsilon})\,Y_{\ell' m'}(\hat{\epsilon}') \qquad (9)$$

where

$$B^{\lambda\lambda' o \ell\ell'}_{\mu_j\mu_j o mm'} = \langle Y_{\lambda\mu_j}(\hat{r}) \,|\, Y_{\ell m}(\hat{r})\, Y_{\ell' m'}(\hat{r}) \,|\, Y_{\lambda'\mu_j}(\hat{r}) \rangle$$

is a special case of Eq. (6) and ξ's are defined as in Eq. (7). Finally the expression for the transition amplitude is obtained by combining Eqs. (8), (9) and (3):

$$T_{fi}^{(n,l)} = \langle \chi_{v_f}(R) \,|\, \sum_{\text{all } p,q} N^{(R)}_{n-p_o, l-q_o} \prod_{j=1}^{N-1} M^{(R)}_{p_{j-1}-p_j,\, q_{j-1}-q_j} M^{(R)}_{p_{N-1} q_{N-1}} \,|\, \chi_{v_i}(R) \rangle \qquad (10)$$

where the summations are, in general, over all integer p's and q's in the range $-\infty$ to $+\infty$. (It is of some interest to note that for a one electron molecule N = 1 (e.g. H_2^+, DH^+ etc.) the intermediate product over j is replaced by unity and the summations reduce to that over p_o and q_o only).

In the above we have thus reduced the calculation of any given transition amplitude to that of radial matrix elements (which can be evaluated numerically) and their summations which is convenient to program. The expression for any degeneracy averaged probability of transition can be written down by multiplying Eq. (10) with its complex conjugate and summing over the final and averaging over the initial magnetic substates. However, experience shows that in actual computation it is more convenient to deal with the amplitude itself and perform the above operations in the machine with the help of standard subroutines to handle angular momentum algebra no more complicated than Clebsh-Gordan coefficients. Finally we point out that the summations over the q's in Eq. (10) can be truncated readily for practical computations by keeping terms

only up to the first order in the weak field strength a′, since these are the only terms which contribute significantly.

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REFERENCES

1. P. Agostini, M. Lu Van and G. Mainfry, Phys. Lett., 36A, 21, (1971).
H. B. Bebb and A. Gold, Phys. Rev., 143, 1, (1965).
E. Karule, J. Phys. B: Atom. Molec. Phys., 4, L67 (1971).

2. H. R. Reiss, Phys. Rev. A, 1, 803 (1970).
_____Phys. Rev. Lett. 25, 1149 (1970).
_____Transitions in Electromagnetic Fields of Arbitrary Intensity (The American University, Preprint, July 9, 1971). We wish to thank Professor Reiss for the above preprint where his closed form results are derived, and also for bringing Ref. 1 to our notice.

3. The validity of such an approximation for bound state electrodynamics has been discussed by Reiss (See. Ref. 2).

4. Wilson, Decius and Cross, Molecular Vibrations, (McGraw Hill, 1955).

5. We have included a weak field photon of frequency ω' in this expression in the manner of Ref. 2.

6. I. S. Gradshteyn and I. M. Ryshik, Table of Integrals, Series and Products, (Academic Press, 1965), p. 980.

7. See Ref. 6, p. 952.

8. M. Abramovitz and I. A. Stegun, Handbook of Mathematical Functions, N. B. S., Washington, D.C., 1964, p. 438.

9. See Ref. 6, p. 684. See also p. 690 (6.569) for an alternative result in terms of summations of ${}_2F_3$ hypergeometric functions.

10. See Ref. 6, p. 985.

11. F. H. M. Faisal, J. Phys. B: Atom. Molec. Phys., 3, 636 (1970).

12. Calculation with determinental wave functions can be done in a similar way without difficulty. (See Ref. 11).