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Electric Dipoles in Atoms and Molecules and the Stark Effect

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Electric Dipoles of Atoms and Molecules and the Stark Effect

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Abstract.
   This article was written for undergraduate and postgraduate students of physics. We analyze the *electric dipole moments* (EDM) of atoms and molecules when they are isolated and when are placed in a uniform static electric field. This was done this because usually in text books and articles this separation is not clearly displayed.
Key words: Electric dipole moments of atoms and molecules; Stark effect.

(I) Introduction.

   Our goal is to write an article for undergraduate and postgraduate students of physics to study the *electric dipole moments* (EDM) of atoms and molecules when they are **isolated** and when they are placed in a uniform static **electric field**. We have done this because many times in text books and articles this separation is not clearly displayed. The dipole of an isolated system will be named *natural or permanent* EDM and that one which is generated by an external field will be named *induced* EDM.

   So, we begin recalling the definition of EDM adopted in basic physics courses[1–4] for an **isolated** aggregate of charges. If in a given system positive charges $+ q$ and negative $-q$ are concentrated at different points we say that it has an EDM. It is mathematically defined by the vector $\mathbf{p} = q\mathbf{d}$, where $\mathbf{d}$ is the distance between the centers of charges positively oriented from $-q$ to $+ q$.

   In general case, in classical electrodynamics,[5,6] $\mathbf{p}$ is defined by

$$\mathbf{p} = \int_V d\mathbf{r}\ \mathbf{r}\ \rho(\mathbf{r}) \qquad\qquad (I.1),$$

where $\rho(\mathbf{r})$ is the charge density and V is the volume of the system. From (I.1) we see that $\mathbf{p} = 0$ or $\mathbf{p} \neq 0$ depending on the charge distribution $\rho(\mathbf{r})$.

   Let us consider the simplest case of the hydrogen−like atom where a single eletron describes, according to classical mechanics,[7,8] an elliptical orbit $\mathbf{r} = \mathbf{r}(t)$ around a nucleus which is at the origin of the coordinate system. In this case the EDM of the atom $\mathbf{p(t)} = e\ \mathbf{r}(t)$, where e is the electron charge, depends on the time t. In spite of $\mathbf{p(t)} \neq 0$ for each time t its

average value $< \mathbf{p}(t) > = < \mathbf{p} > = 0$. The expected (or observed) EDM value is $< \mathbf{p} > = 0$ because the effective center of negative charges coincides with the center of positive charges, the nucleus. As will be seen in section 1, within the framework of quantum mechanics, depending on the atomic state we can have $< \mathbf{p} > \neq 0$.

In quantum mechanics[9–12] an atom or molecule is represented by a wavefunction $|\Psi(\mathbf{r}) >$ which obeys the equation $H_o |\Psi(\mathbf{r}) > = E |\Psi(\mathbf{r}) >$, where H_o and E are, respectively, the Hamiltonian operator and the energy of the isolated system. The expected (average) value $< \mathbf{p} >$ in the state $|\Psi(\mathbf{r}) >$ is defined by

$$< \mathbf{p} > = \int_V d\mathbf{r}\ \Psi^*(\mathbf{r})\ \mathbf{r}\ \Psi(\mathbf{r}) = < \Psi(\mathbf{r})|\ \mathbf{r}\ |\ \Psi(\mathbf{r}) > \qquad (I.2).$$

Since $P\mathbf{r} = - \mathbf{r}$, where P is the parity operator we verify from (I.2) that $< \mathbf{p} > = 0$ if $|\Psi(\mathbf{r})>$ has a definite parity, that is, if $P|\Psi(\mathbf{r})> = +|\Psi(\mathbf{r})>$ or $-|\Psi(\mathbf{r})>$. The EDM can be $< \mathbf{p} > \neq 0$ only when $|\Psi(\mathbf{r})>$ does not have a definite parity.

In Section 1 the EDM of the **isolated** hydrogen−like atom will be calculated in the non−relativistic and the relativistic quantum approaches. It will be shown that $< \mathbf{p} > = 0$ for the *nondegenerate* energy ground−state and that $< \mathbf{p} > \neq 0$ only for *degenerate* excited states. When $< \mathbf{p} > \neq 0$ the EDM is called *natural or permanent*. This feature is found not only for the hydrogen−like atoms but also for all multielectron atoms[10–12] as will be commented at the end of Section 1.

Even though the total charge of an **isolated molecule** is zero, the nature of chemical bonds is such that the positive and negative charges do not completely overlap in most molecules. These non-uniform distributions of positive and negative charges, with different electronegativity, can create *permanent* electric dipoles, that is, $< \mathbf{p} > \neq 0$ at molecular ground−states.[13] Molecules with *permanent* EDM are called *polar molecules* like H_2O,[14] HF,…, NaCl. In Section 2 we present a simple model to explain the existence of natural EDM in ground states of polar molecules.[13,14] It will be also calculated the expected values of these EDM for spherical and symmetrical top molecules turning freely in the space. In Section 3 we study the EDM of free polar molecules.

Even if atoms and non polar molecules do not have *natural* EDM it is possible to induce dipoles by the application, for instance, of a static electric field $\mathbf{E}$. These dipoles are called *induced* EDM. $\mathbf{E}$ produces a shift of the energy levels of the systems known as *Stark effect*[10–12] that will studied in Section 4.

Following the procedure adopted in our preceding didactical papers a number minimum of references (articles and books) will be cited.

Many sensitive experiments have been developed to search EDM of atoms, molecules and elementary particles.[15] These experiments are of fundamental importance in order to decide which of the myriad theoretical models correctly describes violations of time−reversal (T) invariance that have been observed in the in the $K_2^o \rightarrow 2\pi$ decay. It is known that the existence of EDM on an elementary particle would violate both parity (P) and time−reversal invariances.[15] Since the parity is well known to be violated there is no reason why an elementary particle should not have a *natural* (or *intrinsic*) EDM. This situation has stimulated considerable interest for search of the intrinsic EDM of elementary particles. Much theoretical and experimental research has been performed[15] to determine the intrinsic d_e of electrons. The present experimental upper limit on d_e is $|d_e| \leq 1.6 \ 10^{-27}$ e cm.[15]

The analysis to search EDM of atoms, molecules and elementary particles can be performed assuming from beginning the CPT symmetry principle.[15] In this paper we take into account only the parity operation.

(1) EDM of Isolated Hydrogen−like and Multielectrons Atoms.

The parity operator P introduced in quantum mechanics,[10−12] which has no classical analogue, is defined as an operator that reflects the coordinates of all particles through the origin:

$$Pf(\mathbf{r}_1, \mathbf{r}_2, \ldots, t) = f(-\mathbf{r}_1, -\mathbf{r}_2, \ldots, t) \qquad (1.1).$$

From (1.1) we see that P^2 is the unit operator 1. Note that Pf is not necessarily equal to $\pm$ f, that is, f can have an *indefinite* parity. Functions with definite parity obey the condition Pf = + f or Pf = − f.

Indicating by $|\Psi(\mathbf{r}_i)\rangle$ the energy eigenfunction of the isolated atom where $\mathbf{r}_i$ are the positions of the ith electrons relative to the nucleus the expected EDM value for the atom in the state $|\Psi(\mathbf{r}_i)\rangle$, according to (I.2), is given by

$$< \mathbf{p} > = < \Psi | \mathbf{p} | \Psi > = \int |\Psi(\mathbf{r}_i)|^2 \mathbf{p} \ dV_N \qquad (1.2)$$

where $\mathbf{p} = e\Sigma_{i=1,\ldots,N} \mathbf{r}_i$ and is N the total number of the electrons in the atom. Thus, for states $|\Psi(\mathbf{r}_i)\rangle$ with well *definite parities* that is, when $P|\Psi(\mathbf{r}_i)\rangle = +$ $|\Psi(\mathbf{r}_i)\rangle$ or $- |\Psi(\mathbf{r}_i)\rangle$, since $P\mathbf{p} = -\mathbf{p}$, the observed EDM value (1.2) for these states is null , that is, $< \mathbf{p} > = 0$. When $|\Psi(\mathbf{r}_i)\rangle$ does not have a definite parity $< \mathbf{p} >$ is not necessarily equal to zero.

(1.1) *Hydrogen−like atom:Non−Relativistic Approximation*

Before to calculate the EDM of an **isolated** hydrogen−like atom let us recall the definition of degenerate and non−degenerate energy level in quantum mechanics.[9−12] Let us indicate by H_o, u_n and E_n the Hamiltonian,

the energy eigenfunctions and eigenvalues, respectively, of the atom or molecule. The energy level E_n is named f–fold degenerate when there are f different eigenfunctions $\{u_{nk}\}_{k=1,2,...,f}$ with the same energy E_n. The energy spectrum is said non–degenerate when to a given function u_n corresponds only one eigenvalue E_n, that is, when $f = 1$.

Now we are in condition to answer the following question: for what kind of states the parity is well definite? To do this we begin analyzing the hydrogen–like atom in the non–relativistic approximation. In this case its energy eigenstates are given by $|n\ell m> = \Psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi)$.[9–12]

The ground-state $|100>=R_{no}(r)Y_{oo}(\theta,\varphi)=R_{no}(r)/\sqrt{4\pi}$ is non–degenerate with a positive parity, remembering that[5,6] $PY_{\ell m}(\theta,\varphi)=(-1)^{\ell}Y_{\ell m}(\theta,\varphi)$. Consequently, according to (1.2), the average EDM of the hydrogen in the ground–state is given by

$$< \mathbf{p} >_{11} = (e/4\pi) \int r^3\, |R_{no}(r)|^2\, dr \int_{4\pi} \boldsymbol{r}\, d\Omega = 0 \qquad (1.1.1),$$

where $\boldsymbol{r} = \mathbf{r}/r$ is the radial unit vector and Ω is solid angle.

Now, let us consider the first excited state $n = 2$ which is a 4–fold degenerate energy eigenstate.[9–12] So, the $n = 2$ state Ψ_2 would be given, in the general case, by a linear superposition of the components $|200>$, $|210>$, $|21+1>$ and $|21-1>$, that are shown explicitly elsewhere.[10–12] Supposing, for instance, that Ψ_2 is only given by $\Psi_2 = (|200> + |210>)/\sqrt{2}$, since the diagonal matrix elements $<200|\mathbf{d}|200>$ and $<210|\mathbf{d}|210>$ are equal to zero, we get

$$< \mathbf{p} >_{22} = < \Psi_2|\, \mathbf{d}\, |\, \Psi_2 > = <200|\, e\, r\cos\theta\, |210 >\, \boldsymbol{z}\ =$$

$$\qquad (1.1.2),$$

$$= e \int R_{20}(r)\, R_{21}(r)r^3 dr \int d\Omega \cos\theta\, Y_{0,0}(\theta,\varphi)Y_{1,0}(\theta,\varphi) = 3ea_o\boldsymbol{z} \neq 0$$

where a_o is the Bohr radius and $\boldsymbol{z}$ is unit vector along the z axis. Similarly, we can be shown that $< \mathbf{p} >_{nn}$ may be non null for other hydrogen excited states n. According to (1.1.2) the order of magnitude of the EDM for the $n = 2$ excited state is $\sim e\, a_o = 5\ 10^{-9}$ e cm.

(1.2) *Hydrogen–like Atom*: *Relativistic Approximation.*

Using Dirac´s equation the stationary states wavefunctions of one electron in a Coulomb field are given by[11]

$$\Psi_{n\ell jm} = |n\ell jm> = \psi_{nj}(r)\, \Phi_{\ell 1/2 jm}(\theta,\varphi) \qquad (1.2.1),$$

where the radial functions $\psi_{nj}(r)$ are in the zeroth approximation the same functions $R_{n\ell}(r)$ of the non–relativistic Schrödinger´s equation for a spinless particle.[11,12] The generalized angular momentum functions

$\Phi_{\ell 1/2 jm}(\theta,\varphi)$ which take into account the total angular momentum j, its the z−component m, the orbital angular momentum ℓ and the spin ½ functions $\chi_{\frac{1}{2} m_s}$ are given by[11,16]

$$\Phi_{\ell 1/2 jm}(\theta,\varphi) = \sum_{m_s = 1/2, -1/2} (\ell, 1/2, m-m_s, m_s \mid jm) Y_{\ell, m-m_s}(\theta,\varphi) \chi_{\frac{1}{2} m_s} \qquad (1.2.2),$$

where $(\ell, m-1/2, m-m_s, m_s \mid jm)$ are the Clebsch−Gordan coefficients[11,17−19] and $\chi_{\frac{1}{2} m_s}$ are the two components spin functions, for $m_s = +1/2$ and $-1/2$,

$$\chi_{\frac{1}{2}, \frac{1}{2}} = \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_{\frac{1}{2}, -\frac{1}{2}} = \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The wavefunctions (1.2.1) are simultaneously eigenfunctions of H_o, $\mathbf{J}^2$, $\mathbf{s}^2$ and $\mathbf{L}^2$ with the following eigenvalues:

$$E_{nj} = - (\mu Z^4 e^4 / 2\hbar^2 n^2)\{1 + (\alpha^2/n)[1/(j + 1/2) - 3/(4n)], \quad \alpha = e^2/\hbar c,$$

$$L^2 = \hbar^2 \ell(\ell+1), \quad \ell = 0,1,\ldots, n-1 \qquad\qquad (1.2.3).$$

$$J^2 = \hbar^2 j(j+1), \quad j = \ell \pm \tfrac{1}{2}, \quad m = -j, -j+1,\ldots, j-1, j \quad \text{and} \quad s^2 = 3\hbar^2/4$$

Taking into account the Clebsch−Gordan coefficients[17,18] and that $\ell = j \pm \frac{1}{2}$ the function (1.2.1) are written as[16]

(a) $j = \ell + \frac{1}{2}$

$$u_- = \Psi_{n \ell\, j= \ell+1/2\, m} = [R_{n,j-1/2}(r)/\sqrt{(2j)}] \begin{pmatrix} \sqrt{(j+m)}\ Y_{j-1/2, m-1/2} \\ \sqrt{(j-m)}\ Y_{j-1/2, m+1/2} \end{pmatrix}$$

$$(1.2.4)$$

(b) $j = \ell - \frac{1}{2}$

$$u_+ = \Psi_{n \ell\, j= \ell-1/2\, m} = [R_{n,j+1/2}(r)/\sqrt{(2j+2)}] \begin{pmatrix} \sqrt{(j+1-m)}\ Y_{j+1/2, m-1/2} \\ -\sqrt{(j+1+m)}\ Y_{j+1/2, m+1/2} \end{pmatrix}$$

For the ground−state n =1, $\ell = 0$ only j = ½ is possible. For these quantum numbers, since m = ½ and − ½, we verify that there are two functions $\Psi_{1\, 0\, 1/2\, 1/2}$ and $\Psi_{1\, 0\, 1/2\, -1/2}$ for the ground-state, both with the same energy $E_{1\,\frac{1}{2}}$ given, respectively, by

$\Psi_+ = \Psi_{1\,0\,1/2\,1/2} = R_{10}(r)\ Y_{oo}(\theta,\varphi)\ \chi_+ = (R_{10}(r)/\sqrt{4\pi})\ \chi_+$ (spin up),

(1.2.5).

$\Psi_- = \Psi_{1\,0\,1/2\,-1/2} = R_{10}(r)\ Y_{oo}(\theta,\varphi)\ \chi_- = (R_{10}(r)/\sqrt{4\pi})\ \chi_-$ (spin down)

and
$$E_{1\,1/2} = E_1(Bohr)\{1 - Z^2\ \alpha^2\}$$

For the *first excited state* n = 2 there are the following possibilities

n = 2, $\ell = 0$, j = ½ $\rightarrow$ $\Psi_{2\,0\,1/2\,m}$ $\rightarrow$ $E_{2\,\frac{1}{2}} = E_1(Bohr)\{1 - 5Z^2\alpha^2/16\}$

n = 2, $\ell = 1$, j = ½ $\rightarrow$ $\Psi_{2\,1\,1/2\,m}$ $\rightarrow$ $E_{2\,\frac{1}{2}} = E_1(Bohr)\{1 - 5Z^2\alpha^2/16\}$ (1.2.6)

n = 2, $\ell = 1$, j = 3/2 $\rightarrow$ $\Psi_{2\,1\,3/2\,m}$ $\rightarrow$ $E_{2\,3/2} = E_1(Bohr)\{1 - Z^2\alpha^2/16\}$

where the functions Ψ seen above can be constructed using (1.2.4). The level $E_{2\,3/2}$ is 5−fold degenerate since m = −3/2, −1/2, 0, 1/2, 3/2. The level $E_{2\,\frac{1}{2}}$ is 4−fold degenerate being represented by 4 different states $\Psi_{2\,0\,1/2\,m}$ and $\Psi_{2\,1\,1/2\,m}$ with m = +1/2 and −1/2. Note that the levels $2s_{1/2}$ and $2p_{1/2}$ are shifted with respect to one another by ~1040 Megacycles[20] (microwave region). This shift which is called *Lamb−shift* is explained by the quantum electrodynamics.[20]

Using (1.2.5) we verify that for the relativistic hydrogen ground−state n =1 the EDM expected value $< \mathbf{p} >_{11} = 0$ because

$< \Psi_+| \mathbf{r} | \Psi_+ > = < \Psi_-| \mathbf{r} | \Psi_- > = < \Psi_+| \mathbf{r} | \Psi_- > = < \Psi_-| \mathbf{r} | \Psi_+ > = 0$ (1.2.7).

Now, let us calculate the expected value of the EDM for the degenerate excited states n > 1. For simplicity we calculate the EDM only along the z−axis, that is, $< p_z > = e < z > = e < r \cos\theta >$. This value will be obtained calculating the matrix elements $< u_-| z |u_- >$, $< u_+| z |u_+ >$ and $< u_+| z |u_- > = < u_-| z |u_+ >$, where u_- and u_+ are given by (1.2.4):

$< u_-| z |u_- > = \int R_{n,j-1/2}(r)^2 r^3 dr/(2j)\ \{\ (j+m)\int d\Omega \cos\theta\ |Y_{j-1/2,m-1/2}|^2 +$

$+ (j-m)\int d\Omega \cos\theta\ |Y_{j-1/2,m+1/2}|^2\ \}$

$< u_+| z |u_+ > = \int R_{n,j+1/2}(r)^2 r^3 dr/(2j)\ \{\ (j-m)\int d\Omega \cos\theta\ |Y_{j+1/2,m-1/2})|^2 +$

$+ (j+m)\int d\Omega \cos\theta\ |Y_{j+1/2,m+1/2}|^2\ \}$

and
(1.2.8)

$$< u_- |\ z\ |u_+ > = \int R_{n,j+1/2}(r)\ R_{n,j-1/2}(r) r^3 dr/(2\sqrt{j(j+1)})\ \times$$

$$\times\ \{\sqrt{(j+m)}\sqrt{(j+1-m)}\ \int d\Omega\ \cos\theta\ Y^*_{j-1/2,m-1/2}\ Y_{j+1/2,m-1/2}\ +$$

$$\sqrt{(j-m)}\sqrt{(j+1+m)}\int d\Omega\ \cos\theta\ Y^*_{j-1/2,m+1/2}\ Y_{j+1/2,m+1/2}\ \}$$

These (1.2.8) matrix elements $< u_- |\ z\ |u_+ > = < u_- |\ z\ |u_+ >$ are calculated between the states n, j, m, $\ell = j + \frac{1}{2}$ and n, j, m, $\ell = j - \frac{1}{2}$. . Since [11,16]

$$\cos\theta\ Y_{\ell,m}(\theta,\varphi) = [(\ell+1+m)(\ell+1-m)/(2\ell+1)(2\ell+3)]^{1/2}\ Y_{\ell+1,m}(\theta,\varphi)$$

$$(1.2.9)$$

$$+\ [(\ell+m)(\ell-m)/\ (2\ell+1)(2\ell-1)]^{1/2}\ Y_{\ell-1,m}(\theta,\varphi)$$

it is not difficult to verify that these matrix elements are equal to zero between states with different m values and that the diagonal elements $< u_- |\ z\ |u_- >$ and $< u_+ |\ z\ |u_+ >$ are also null. We also can also shown that the expression within the braces of $< u_- |\ z\ |u_+ >$ in (1.2.8) is equal to

$$[(j+m)(j-m+1)-(j+m+1)(j-m)]/\ 2\sqrt{j(j+1)}) = m/\sqrt{j(j+1)}).$$

Integrating the radial part of (1.2.8) taking into account the hydrogen wavefunctions [10-12] $R_{n\ell}(r)$ we get

$$-\ (3/2)\ n\ [n^2 - (j +1/2)^2]^{1/2}.$$

Finally, the matrix element $< u_- |\ z\ |u_+ >$ becomes given by

$$<\Psi_{n\ j\ \ell=j+1/2\ m}|\ z\ |\Psi_{n\ j\ \ell=j-1/2\ m}> = -(3/4)a_o\ n\ m\ [n^2 -(j +1/2)^2]^{1/2}/[j(j+1)]\ (1.2.10).$$

Note that the energy levels E_{nj} described by the eigenfunctions u_+ and u_- defined by (1.2.4) are *f*–fold degenerate: 2–fold degenerate with respect to ℓ and $\ell\pm1$ and 2(j+1) with respect to m (see (1.2.3)).

Assuming that the n = 2 degenerate state is represented by the superposition of the two states with n = 2, j =½, ℓ = 1, m = −1/2 and n = 2, j = ½, ℓ = 0, m = −1/2, that is, $\Psi_2 = (\Psi_{2\ \frac{1}{2}\ 1\ -1/2}\ +\ \Psi_{2\ \frac{1}{2}\ 0\ -1/2})/\sqrt{2}$ we can use (1.2.10) to calculate the z–component of the EDM,

$$< p_z >_{22} =\ \ e < \Psi_2|\ z\ |\Psi_2> =\ e\ \sqrt{3}\ a_o\ \neq 0 \qquad (1.2.11)$$

We can also calculate $<p_z>_{22}$ putting in (1.2.4) n = 2, j =½, ℓ = 0 and m = −1/2:

$$u_- = \Psi_{2\,1/2\,0\,-1/2} = [R_{20}(r)/\sqrt{1}] \begin{pmatrix} \sqrt{0}\ Y_{0,-1} \\ \sqrt{1}\ Y_{0,0} \end{pmatrix}$$

and n = 2, j =½, ℓ = 1 and m = −1/2,

$$u_+ = \Psi_{2\,1/2\,1\,-1/2} = [R_{21}(r)/\sqrt{3}] \begin{pmatrix} \sqrt{2}\ Y_{1,-1} \\ \sqrt{1}\ Y_{1,0} \end{pmatrix}$$

we get, using (1.2.8),

$$< p_z >_{22} = e < \Psi_2 | \, r\cos\theta \, |\Psi_2> =$$

$$= e \int R_{20}(r)\,R_{21}(r)r^3 dr/(\sqrt{3}\sqrt{1}) \int d\Omega \cos\theta\, Y_{0,0}(\theta,\varphi)\, Y_{1,0}(\theta,\varphi) = e\,\sqrt{3}\,a_o \neq 0,$$

which is the same result shown by (1.2.11).

     Finally, let us comment about the *hyperfine structure* due to the interaction of the magnetic moment **μ** ("Zeeman effect") of the nucleus with the total angular momentum **J** of the orbital electrons.[11] Since the nuclear momentum **μ** is around 10^3 smaller than orbital magnetic moment of the electron this nuclear effect produces an energy splitting about 10^3 smaller than the splitting due to spin−orbit interaction (the fine structure). The atomic ground state energies are only slightly decreased and the respective s−functions are only slightly modified.[11] The hyperfine structure effect is so small that the value $< \mathbf{p} >_{11} = 0$ is not modified for the atomic ground−states.

     So, for the hydrogen−like atom we verified that $<\mathbf{p}>_{11} = 0$ for the ground−state (*nondegenerate state)* and that it can be $<\mathbf{p}>_{nn} \neq 0$ for excited states n >1 *(degenerate states).* That is, only *excited states* can have *natural* dipole moments.

(1.3) *Multielectron Atoms.*

     Many extensive theoretical and experimental studies that have been performed for multielectron atoms[12] have shown that all ground−states of all atoms (and nuclei) are very likely to be nondegenerate and that atoms (and nuclei) in its ground−states do not possess *natural* EDM, and none has ever been found experimentally. Only a degenerate state may, in general, have a non−vanishing $< \mathbf{p} >$, provided the state has not got a well defined parity. So, only excited atomic states can have a *natural* EDM.

     In multielectron atoms the field acting upon an electron is, in general, different from the Coulomb field and the levels pertaining to different ℓ (and thus with different parity) always have different energies. The average EDM vanishes in these states. An interesting case extensively studied is that of the alkali atoms.[12,21] The ground−state configuration

consists of a series of full shells followed by a single s electron. The inner rare−gas configuration is so stable that all but quite high excited states of the atom involve only the valence electron. Thus, alkalis can be treated to quite good approximation in terms of a model in which a single electron moves in a spherically symmetric non−Coulomb potential V(r) with an additional spin−orbit interaction **L·S**. The EDM in alkali atoms has been extensively studied[21] in order to verify the existence of an intrinsic EDM of the electrons.

(3) EDM of Isolated Polar Molecules.

As explained in the Introduction, even though the total charge of **isolated** molecules is zero, the nature of chemical bonds is such that the positive and negative charges do not completely overlap in most molecules.[13,14] These non−uniform distributions of positive and negative charges on the various atoms can create *permanent* electric dipoles, that is, < **p** > ≠ 0 in molecular ground−states. Molecules with *permanent* EDM are called *polar molecules*. First we present a simple model to explain the origin these EDM in polar molecules. After we calculate the expected values of these EDM assuming that the polar molecules are freely rotating rigid bodies. Electronic and vibrational effects will be neglected and only *spherical top* and *symmetrical top* molecules will be studied.

Let us explain qualitatively (since the exact description would involve a many body theory) how can be formed a permanent EDM in the simplest case of diatomic molecules.[13] We assume that the two centers of charges +q and −q, created by the exchange of electrons between the atoms of the molecule, like in the heteropolar bonding, are separated by distance r. Between these two centers there is a Coulomb potential $V(r) = -q^2/r$ at large distances r > R. At short distances r < R due to the interpenetration of the electronic clouds involving the charges + and −, there appear a strong repulsive potential U(r) for r → 0. In this way the two atoms move submitted to an effective potential $V_{eff}(r) = U(r) + V(r)$. This potential $V_{eff}(r)$ which is responsible for the atomic bonding, has a minimum at a certain point r_{min} around of which the two atoms oscillate harmonically[10−12] with frequency ω and energies $E_n = (n + 1/2)\hbar\omega$. The average distance r between the atoms increases as n increases but at the ground−state n = 0 this distance assumes the minimum average value r_{min}. Thus, at the ground−state the dipole moment of the molecule is $p = e\, r_{min} \neq 0$.

We recall that in classical mechanics the rotational energy E of a rigid body is given by the equation [7,11]

$$E = [L_\xi^2/I_\xi + L_\eta^2/I_\eta + L_\zeta^2/I_\zeta]/2 \qquad (3.1),$$

where $\xi\eta\zeta$ is the system of coordinates (principal axes of inertia) in the rigid body and the orientations of the body is determined by angles of Euler $\alpha\beta\gamma$ which characterize the position of the $\xi\eta\zeta$–axes with respect with the laboratory xyz–system; I_ξ , I_η and I_ζ are the principal moments of inertia and L_ξ ,L_η and L_ζ are the components of the angular momentum along the $\xi\eta\zeta$–axes, respectively. In quantum mechanics the angular momentum components L_ξ, , L_η and L_ζ will be substituted by the angular momentum operators J_ξ, J_η and J_ζ and the Hamiltonian operator H is written as

$$H = (aJ_\xi{}^2 + bJ_\eta{}^2 + cJ_\zeta{}^2)/2 \qquad (3.2),$$

where $a = 1/I_\xi$, $b = 1/I_\eta$ and $c = 1/I_\zeta$ and the operators J_ξ, J_η and J_ζ obey the commutation relations $[J_\xi, J_\eta] = -i\hbar J_\zeta$,…. Note that in (3.2) we have used the angular momentum **J** instead of **L** because in the general case **J** represents the total angular momentum of the molecule which is given by the sum of the rotational angular momentum, the electronic angular momentum and the spin of the molecular components.

(3.1) *Spherical Top*.
A rigid body is called spherical top[7,11] when it has three equal moments of inertia $a = b = c = I^{-1}$. In this case the Hamiltonian (3.2) becomes

$$H = \mathbf{J}^2/2I \qquad (3.3).$$

The eigenfunctions $|jmk> = \psi^j{}_{mk}(\alpha\beta\gamma)$ and eigenvalues E_j of H are given by[11,16,17]

$$H \,|jmk> = E_j \,|jmk> = [\hbar \, j(j+1)/2I] \,|jmk>$$

where

$$|jmk> = \psi^j{}_{mk}(\alpha\beta\gamma) = \sqrt{(2j+1)/8\pi^2} \, D^j{}_{mk}(\alpha\beta\gamma) \qquad (3.4),$$

$$D^j{}_{mk}(\alpha\beta\gamma) = \exp(im\alpha) \, d^j{}_{mk}(\theta) \, \exp(ik\gamma)$$

with

$$k, m = 0, \pm 1, \pm 2,..., \pm j$$

which implies that for each eigenvalue E_j the energy levels $j \neq 0$ are $2(2j+1)$–fold degenerate. The functions $D^j{}_{mk}(\alpha\beta\gamma)$ that are called *generalized spherical functions* describe finite rotations over the Euler angles $\alpha\beta\gamma$ of the system of coordinates $\xi\eta\zeta$ with respect to the laboratory system of coordinates xyz. They obey the following conditions [11,17,18]

$$\mathbf{J}^2 \, D^j_{mk} = \hbar \, j(j+1) \, D^j_{mk} \, , \qquad J_\zeta \, D^j_{mk} = \hbar \, k \, D^j_{mk}$$

(3.5).

$$J_z \, D^j_{mk} = \hbar \, m \, D^j_{mk} \quad \text{with} \quad \langle jmk|j'm'k'\rangle = \delta_{jj'} \, \delta_{mm'} \, \delta_{kk'}$$

(3.5) shows that $\hbar k$ is the **J**−component along the ζ−axis and that $\hbar m$ is the **J**−component along the z−axis. Note that the polar coordinates (φ,θ) with respect to the original frame S (laboratory) of the z−axis in its final position are identical with the Euler angles (α,β), respectively.[17]

Since j = integer = ℓ if k = 0 or m = 0 we have,[11,17,18]

$$\langle jm0| = \langle \ell m| = D^\ell_{mo} = [4\pi/(2\ell+1)]^{1/2} \, Y^*_{\ell m}(\theta,\varphi)$$

(3.6)

$$\langle j0k| = \langle \ell k| = D^\ell_{ok} = [4\pi/(2\ell+1)]^{1/2} \, Y_{\ell k}(\theta,\varphi)$$

where θ is the angle between the axes z and ζ and φ is the angle between the projection of the ζ−axis in the xy plane and the x−axis.

The spherical functions D^j_{mk} obey the following property[11,17,18,24]

$$\int d\Omega \, D^J{}^*_{MK}(\theta) \, D^j_{mk}(\theta) \, D^v_{rq}(\theta) = [8\pi^2/(2j+1)] \, (jvmr|JM)(jvkq|JK) \quad (3.7),$$

where $\theta = (\alpha,\theta,\gamma)$ and $d\Omega = \sin\theta \, d\theta \, d\alpha \, d\gamma$. For the spherical top molecules since j = ℓ, we have $D^j_{mk}(\theta) = D^\ell_{mk}(\theta) = |\ell mk\rangle$.

Putting ζ−axis along the dipole **p** its xyz components will be $p_z = p \cos\theta$, $p_x = p \sin\theta \cos\varphi$ and $p_x = p_\zeta \sin\theta \sin\varphi$. In this way, their average values are given by $p \, \langle \ell mk|\cos\theta|\ell mk\rangle$, $p \, \langle \ell mk|\sin\theta\cos\varphi|\ell mk\rangle$ and $p \, \langle \ell mk|\sin\theta\sin\varphi \, |\ell mk\rangle$. Using (3.7) we verify that $\langle \ell mk|\cos\theta|\ell mk\rangle = \langle \ell mk|\sin\theta\cos\varphi|\ell mk\rangle = \langle \ell mk|\sin\theta\sin\varphi|\ell mk\rangle = 0$. Consequently, for a freely rotating *spherical top polar molecule* we have always

$$< \mathbf{p} > = 0. \tag{3.8}.$$

(3.2) *Symmetrical Top.*

For a symmetrical top[7,11] which has a = b $\neq$ c the Hamiltonian of the free molecule (3.2) is written as

$$H = [a\mathbf{J}^2 + (c - a)J_\zeta{}^2]/2 \tag{3.9},$$

where $c = b = 1/I_\eta = 1/I_\xi$ and $a = 1/I_\zeta$ choosing the ζ−axis as the symmetry axis of the molecule named *axis of the top*. One can verify that the eigenfunctions[11,17,18] of (3.9) are $|jmk\rangle = \psi^j_{mk}(\alpha\beta\gamma)$ defined by (3.4) and have energy eigenvalues $E_{j|k|}$ given by

$$E_{j|k|} = \hbar^2 [a\,j(j+1) + (c-a)k^2] \qquad (3.10).$$

There are $j + 1$ sublevels for each value of j with different energies and $|k| = 0,1,2,\ldots, j$. The energy levels (3.10) are independent of the value of the quantum number m and of the signal of the quantum number k. If $k \neq 0$ each level is thus $2(2j+1)$–fold degenerate. The two–fold degeneracy with respect to the sign of k, that is, with respect to the sign of the projection of the angular momentum **J** along the ζ–axis occurs because H (3.9) is invariant under a coordinate reflection through the axis of symmetry ζ of the molecule. Let us denote by P_ζ the operator responsible for this reflection.

The eigenfunctions |jmk> are not eigenfunctions of P_ζ but it is easily to verify that the following functions

$$|jmk + > = (\,|jmk > + |jm -k >)/\sqrt{2}$$

and $\qquad (3.11)$

$$|jmk - > = (\,|jmk > - |jm -k >)/\sqrt{2}$$

are simultaneously eigenfunctions of P_ζ and H (3.9) noting that P_ζ |jmk + > = |jmk + > and P_ζ |jmk − > = − |jmk − >. So, since <jmk −| ζ |jmk −> $\neq 0$ a permanent EDM $p_\zeta = e\zeta$ along the symmetry axis of the molecule is not forbidden in the state |jmk − >. Only for k = 0 there is only one kind of spherical function: |j m 0> = |j m 0 + > = $[(2j+1)/8\pi^2]^{1/2}$ D^j_{mo}.

Assuming (to simplify the calculations) that **p** is along the ζ–axis let us obtain the expected value $<p_z>$ along the z–axis which is given by

$$<p_z> = <jmk|p_z|jmk> = p <\cos\theta> = p \int d\Omega \; D^{j*}_{mk}(\theta) \cos\theta \, D^j_{mk}(\theta) \quad (3.12),$$

where $\theta = (\alpha,\theta,\gamma)$ and $d\Omega = \sin\theta \, d\theta \, d\alpha \, d\gamma$. Let us calculate this integral taking into account (3.7) remembering that $\cos\theta = \sqrt{4\pi/3} \; Y_{10}(\theta,\varphi) = D^1_{00}(\theta,\varphi)$, according to (3.6), and using Clebsh–Gordan coefficients[17,18]. We can shown that,[22–24]

$$<p_z> = <jmk|p_z|jmk> = - pkm/[j(j+1)] = - p_\zeta \, m/\sqrt{j(j+1)} \qquad (3.13),$$

where $p_\zeta = pk/\sqrt{j(j+1)}$ is the projection of **p** is along the ζ–axis. This shows that $<p_z>$ is the projection of p_ζ along the z–axis which is null only for k = 0 or m = 0.

(4) Stark Effect: Atoms and Molecules Placed in a Static Electric Field.

The energy levels of systems of charges are shifted when placed in an external static electric field E. This shift is named "Stark Effect". When E is switched on, the Hamiltonian of the atom or molecule becomes given by[10–12]

$$H = H_o - \mathbf{p} \cdot E \qquad (4.1),$$

where H_o is the Hamiltonian of the isolated system. It will be assumed that the perturbation created by the uniform E is weak so that its effects can be calculated using the quantum perturbation theory[9–12] (see Appendix) up to the second order approximation in the operator $\mathbf{p} \cdot E$. For the hydrogen−like atoms the Stark effect can be calculated solving the equation $H\Psi = E\Psi$.[10,25]

We will analyze only the Stark effect on the electronic states of the systems. Let us indicate by $|n\ell jm>$ the electronic eigenfunctions and by H_o and $E_{n\ell jm}$ the corresponding Hamiltonian and eigenvalues for an isolated atom or molecule. Due to E the energy $E_{n\ell jm}$ is modified becoming $\mathcal{E}_{n\ell jm}$. Up to the second order approximation, (see Appendix, putting $v = \mathbf{p} \cdot E$ and $u_n = |n\ell jm>$) $\mathcal{E}_{n\ell jm}$ is given by, choosing the z−axis along the field E:

$$\mathcal{E}_{n\ell jm} = E_{n\ell jm} + E \; <n\ell jm| \; p_z \; |n\ell jm>$$

$$+ e^2 E^2 \sum_{n'\ell'j'm'} <n\ell jm|z|n'\ell'j'm'><n'\ell'j'm'|z|n\ell jm>/(E_{nj} - E_{n'j'}) \;(4.2).$$

The first term, proportional to E is called *linear Stark effect* and the second one proportional to E^2 is called *quadratic Stark effect*.

(4.1) *Non−Relativistic Hydrogen−like atom*

For the non−relativistic hydrogen−like atom in accordance with Section 1.1 the expected dipole moment $<n\ell jm|\mathbf{p}|n\ell jm>$ in the ground-state level is equal to zero. So, there is *no linear Stark effect* for the ground-state.

The first excited state n =2 is 4−fold degenerate. This level n = 2 is represented [9–12] by the state functions $\{\psi_i\}_{i=1...4} = \{|210>, |210>, |211>, |21-1>\}$. As is shown in section (A.4) of the Appendix, when the external electric field E is switched on, the 4−fold degenerate level n = 2 is split into three levels. One of these levels with m = ± 1, is 2−fold degenerate: in agreement with the z−symmetry of the problem. The four energy shifts $\mathcal{E}_{n\ell m}$ (see Eq. (A.4.5) of the Appendix) due to the perturbative potential eEz are given by

$$\mathbb{C}_{200} = E_2 + 3eEa_o, \quad \mathbb{C}_{210} = E_2 - 3eEa_o \quad \text{and} \quad \mathbb{C}_{211} = \mathbb{C}_{21-1} = E_2 \qquad (4.3),$$

where $E_2 = -Z^2 e^2 / 2a_o n^2$ is the Bohr energy of the level n = 2. Since the magnitude of the splitting of the levels, according to (4.2), is proportional to *E* the state n = 2 presents a *linear Stark effect*.

(4.2) *Relativistic Hydrogen−like Atom.*

According to Section (1.2) the relativistic energy states |nℓjm> of the hydrogen−like atom are given by $u_- = \Psi_{n\,\ell\,j=\ell+1/2\,m}$ and $u_+ = \Psi_{n\,\ell\,j=\ell-1/2\,m}$ (see (1.2.4)). Taking into account these functions it was shown that for the ground−state level (n = 1) <nℓjm| **p** |nℓjm> = 0. So, there is no *linear Stark effect* for the energy ground−state.

As pointed out in Section (1.2) the energy levels of the excited states u_+ and u_-, for n ≥ 2, are *f*−fold degenerate: 2−fold degenerate with respect to ℓ and ℓ+1 and 2(j+1)−fold degenerate with respect to m. However, since $< u_-|\, z\, |u_-> = < u_+|\, z\, |u_+> = 0$ and $< u_+|\, z\, |u_-> = < u_-|\, z\, |u_+> \neq 0$ we see that the matrix elements between states with ℓ and ℓ+1 and are equal to zero only between states with different m values. In these conditions we easily verify that, in the Stark effect context, the *f*−fold degenerate perturbation approach reduces (see Appendix (A.2)) simply to a 2−fold degenerate case,[16] only for the levels ℓ and ℓ+1. In this way, according to (A.5.1) the energy shift $\mathbb{C}_{n\ell jm}$ due to the perturbation potential e*E*z and using (1.2.10) is given by:

$$\mathbb{C}_{n\ell jm} = E_{n\ell jm} \pm eE< u_-|\, z\, |\, u_+>$$

$$= E_{nj} \pm eE(3/4)a_o\, n\, m\, [n^2 - (j+1/2)^2]^{1/2} / [j(j+1)] \qquad (4.4),$$

using the matrix element (2.10). Eq. (4.4) shows that also in the relativistic approximation the excited states of the hydrogen−like atom present a *linear Stark effect*.

(4.3) *Multielectron Atoms and Non−Polar Molecules.*

The *linear Stark effect* is observed only in a system with a Coulomb potential energy (the hydrogen−like atom) where there is degeneracy with respect to the quantum number ℓ.

In multielectron atoms and molecules the field acting upon an electron is, in general, different from the Coulomb field (see comments at Section 1.3). The electron eigenstates will be represented by |nℓjm>. In these conditions the levels pertaining to different ℓ (and thus with different parity) always have different energies. Since the average EDM vanishes in these states they present no *linear Stark effect*. The influence of *E* will

affect the energy levels only in the second order approximation that according to (4.2) are given as

$$\varepsilon_{n\ell jm} = E_{nj}$$

$$+ e^2 E^2 \sum_{n'\ell'j'm'} <n\ell jm|z|n'\ell'j'm'><n'\ell'j'm'|z|n\ell jm>/(E_{nj} - E_{n'j'}) \quad (4.5).$$

Taking into account that $z = r\cos\theta$ and using (2.9), we verify that

$$\cos\theta \, Y_{\ell,m}(\theta,\varphi) = A \, Y_{\ell+1,m}(\theta,\varphi) + B \, Y_{\ell-1,m}(\theta,\varphi),$$

the z−matrix elements in (4.5) will be non−vanishing only between states for which $\ell' = \ell \pm 1$ and $m' = m$. Consequently, it will remain in the summation (4.5) only the energy shifts $\varepsilon_{n\ell jm}$ depending on m. Taking into account the degeneracy of levels with m and −m we see that the coefficient of proportionality of the energy shift can only be an even function of m. So, we get[10,11]

$$\varepsilon_{n\ell jm} = E_{nj} - e^2 E^2 (\alpha_{n\ell} + \beta_{n\ell} \, m^2)/2 \qquad (4.6),$$

showing a *quadratic Stark effect*.

Let the Hamiltonian H of the system be a function[10] of a parameter λ; its eigenvalues E_n are then functions of λ too. It can be shown that the mean value $<\partial H/\partial\lambda> = <\psi_n|\partial H/\partial\lambda|\psi_n> = \partial E_n/\partial\lambda$. Indeed, to show this let us differentiate $\partial(H - E_n)|\psi_n>/\partial\lambda = 0$:

$$(\partial H/\partial\lambda - \partial E_n/\partial\lambda)|\psi_n> + (H - E_n)(\partial\psi_n/\partial\lambda) = 0.$$

In this way, $<\partial H/\partial\lambda>_{nn} - \partial E_n/\partial\lambda + <\psi_n|(H - E_n)(\partial\psi_n/\partial\lambda)|\psi_n> = 0$. Since H is Hermitean the second term of this last equation is equal to $<\psi_n|(\partial\psi_n/\partial\lambda)|(H - E_n)|\psi_n> = 0$, resulting that $<\partial H/\partial\lambda>_{nn} = \partial E_n/\partial\lambda$.

Considering that the parameter λ is the *E* field the derivative of $H = H_o - E \, p_z$ with respect to it is $- p_z$. Thus, from (4.6) we obtain

$$<p_z>_{nn} = e^2 (\alpha_{n\ell} + \beta_{n\ell} \, m^2)E \qquad (4.7),$$

where $<p_z>_{nn}$ is the *induced EDM* of the system in the state $|\Psi_n>$ and $e^2 (\alpha_{n\ell} + \beta_{n\ell} \, m^2)$ its *polarizability*.

Eq.(4.5) can be written generically as

$$\varepsilon_n^{(2)} = E_n + \sum_{k\neq n} <\Psi_n| \mathbf{p}\cdot\mathbf{E} |\Psi_k><\Psi_k| \mathbf{p}\cdot\mathbf{E} |\Psi_n>/(E_n - E_k)$$

$$= - (1/2) \sum_{i,j=1,2,3} E_i \, \alpha_{ij} \, E_j \qquad (4.8),$$

where α_{ij} is *polarizability tensor* for the $|\Psi_n>$ state is defined by

$$\alpha_{ij} = -2 \sum_{k \neq n} < \Psi_n | p_i | \Psi_k > < \Psi_k | p_j | \Psi_n >/(E_n - E_k) \qquad (4.9),$$

and $< p_i >_{nn}$ in the state Ψ_n is given by $< p_i >_{nn} = \alpha_{ij} E_j$.

　　For atoms, due to a spherical symmetry, the polarizability tensor for atoms is isotropic, that is, $\alpha_{ij} = \alpha_o \delta_{ij}$. Consequently, from (4.7) we get

$$\mathcal{E}_n^{(2)} = E_n - (1/2) \alpha_o E^2,$$

which is the *quadratic Stark shift* for atoms. For many molecules this expression is a good approximation because the molecular tensors α_{ij} are often reasonably isotropic.

(4.4) *Polar Molecules.*

Spherical top molecules.

　　According to Section (3.1) the expected EDM for spherical top polar molecules is $<\ell m| \mathbf{p} |\ell m> = 0$. This means that they do not present *linear Stark effect*. Considering (A.1.2) the second order perturbation Stark shift is written as

$$\mathcal{E}_\ell = E_\ell + e^2 E^2 \sum_{\ell' m'}{'} <\ell m|p_z|\ell'm'>< \ell'm'|p_z|\ell m>/(E_\ell - E_{\ell'}) \qquad (4.10),$$

where $E_\ell = \ell(\ell+1)\hbar^2/2I$ and $|\ell m>$, according to (3.6), is given by $|\ell m> = D^\ell_{om} = [4\pi/(2\ell+1)]^{1/2} Y_{\ell m}(\theta,\varphi)$. Putting $p_z = p \cos\theta$ at (4.10), using (1.2.9) and calculating the matrix elements taking into account that $m' = m$ and $\ell' = \ell \pm 1$ result[24]

$$\mathcal{E}_\ell = E_\ell + (I/\hbar^2) p^2 E^2 \{[\ell(\ell+1) - 3m^2]/[\ell(\ell+1)(2\ell-1) (2\ell+3)]\} \qquad (4.11),$$

showing a *quadratic Stark effect*.

Symmetrical top molecules.

　　According to Section (3.2) the expected EDM value $<jmk| p_z |jmk>$ for symmetrical top polar molecules is given by (3.13):

$$<jmk| p_z |jmk> = - pkm/[j(j+1)].$$

This implies that these molecules present a *linear Stark effect*. Calculating Stark shift up to the second order we get[22-24]

$$\epsilon_{jmk} = E_{jk} - [pkm/(2j+1)]\, E +$$

$$+ (I/\hbar^2)\, p^2 \{[(j2 - m^2)(j^2 - k^2)]/[j^3(2j-1)(2j+1)] -$$

$$[((j-1)^2 - m^2)((j+1)^2 - k^2)]/[(j+1)^3\,(2j+1)(2j+3)]\}\, E^2 \quad (4.12),$$

where E_{jk} is defined by (3.9). Eq.(4.11) shows both *linear* and *quadratic Stark effects.*

Asymmetrical Top Molecules.

Asymmetrical top molecules have three different principal moments of inertia. General principles involved in the motion of such rotors are of course the same as for symmetrical tops, but the details turn out to be much more complex (see Townes and Schawlow[26]). This complexity shows up not only in the quantum−mechanical behavior, but also in its classical motion. The dipole matrix elements and the Stark effect for these molecules can be seen elsewhere.[26]

Appendix. Brief Review of the Stationary Perturbation Theory.

Let us indicate by H_o, u_n and E_n the Hamiltonian, the energy eigenfunctions and eigenvalues, respectively, of an isolated atom or molecule. The level E_n is *f*−fold degenerate when there are *f* different eigenfunctions $\{u_{nk}\}_{k=1,2,\ldots,f}$ with the same energy E_n. The energy spectrum is non−degenerate when to a given function u_n corresponds only one eigenvalue E_n, that is, when *f* =1. Indicating by v the external perturbing potential, the new Hamiltonian is now given by $H = H_o + v$.

According to the usual perturbation theory,[9−12] the new energy eigenfunctions Ψ and eigenvalues ϵ due to the perturbation created by v for non−degenerate and degenerate cases.

(A.1) *Non−Degenerate Case.*

The new eigenfunctions ψ_n and the energies ϵ_n of n states are now given, respectively, by

$$\psi_n = u_n + \Sigma_{n \neq p} <u_p \mid v \mid u_n > u_n /(E_p - E_n) + \ldots \quad (A.1.1),$$

where ψ_n is estimated only up to the first order correction and

$$\mathcal{E}_n = E_n + <u_p|\, v\, |\, u_n> \ + \ \Sigma_{n \neq p}\ |<u_p|\, v\, |\, u_n>|^2/(E_p - E_n) + \dots \qquad \text{(A.1.2)},$$

and the shift of the level $\mathcal{E}_n$ only up to the second order correction.

(A.2) *Degenerate case.*

      In the first step, due to v, the degeneracy of the level is partially or totally removed. Here it will be assumed as totally removed. The case of partial degeneracy lifting can be seen elsewhere.[11,12] So, after obtained these non−degenerate wavefunctions, in a second step, we use them to determine the new functions and energy levels following the procedure used in case (A.1.1) for non-degenerate states. First, let us see how degeneracy is removed. For the f−fold degenerate level E_n we take for the zeroth order the function ψ_n the linear combination[11]

$$\psi_n \ = \ \sum_{k=1,\dots f} a_{nk}\ u_{nk} \qquad \text{(A.2.1)},$$

where u_{nk} satisfies the equation $(H_o - E_n)\, u_{nk} = 0$ e a_k are unknown constants. Substituting ψ_n given by (A.2.1) into the Schrödinger equation with the operator $H = H_o + v$ we obtain a set of f linear, homogeneous equations

$$\sum_{k=1,\dots f} (\ H_{mk} - \mathcal{E}_n\ \delta_{mk})\ a_{nk} \ = \ 0 \qquad (m = 1,2,\dots,f) \qquad \text{(A.2.2)},$$

where $\ H_{mk} = <u_{nm}|\ H\ |\ u_{nk}> \ = \ <u_{nm}|\ H_o + v\ |\ u_{nk}> \ = \ E_n + \ <u_{nm}|\ v\ |\ u_{nk}>.$

      This set of equations has a non−vanishing solution provided the determinant of the coefficients of the unknown a_k a vanishes. From the determinant we get an equation of f−degree for the unknown value of E_n. This equation is called *secular equation* and has f real roots. When all roots are different the f− fold degenerate level E_n is split into f different levels E_{nk} and for each of them we have the corresponding function

$$\psi_{nk} \ = \ \sum_{m=1,\dots f} a_{mk}\ u_{nm} \qquad \text{(A.2.3)},$$

where the coefficients a_{mk} are determined from the equations (A.2.2) after we have substituted for $\mathcal{E}_n$ the value E_{nk}. In this case, when v has completely lifted the degeneracy, the wavefunctions ψ_{nk} belonging to different roots of the secular equation are mutually orthogonal. All off −diagonal elements of H involving the functions ψ_{nk} vanish. So, the

functions ψ_{nk}, in a second step, can be used to calculate the new functions Ψ and energies $\mathbb{C}$ according to the equations (A.1.1) and (A.1.2).

Examples

(A.3) *2−fold degeneracy.*

Let us apply the (A.2) formalism to study the simplest case for a 2−fold degenerate level. In this case, according to (A.2.1), we have $\psi_n = a_{n1} u_{n1} + a_{n2} u_{n2}$. In this way from (A.2.2) we get,

$$(E_n + \mathbb{C}_n + v_{11})a_{n1} - v_{12} a_{n2} = 0$$

(A.3.1)

$$(E_n + \mathbb{C}_n + v_{22})a_{n2} - v_{21} a_{n1} = 0,$$

where a_{ni} are constants. Evaluating the determinant of the secular equation (A.2.2) we find $(E_n + \mathbb{C}_n + v_{11})(E_n + \mathbb{C}_n + v_{22}) + v_{12} v_{21} = 0$. This is a quadratic equation that has two solutions for the energy $\mathbb{C}_n$:

$$\mathbb{C}_n^{(1)} = E_n + v_{11} + v_{12}$$

and

(A.3.2)

$$\mathbb{C}_n^{(2)} = E_n + v_{11} - v_{12} .$$

Substituting $\mathbb{C}_n^{(1)}$ into the first equation (A.3.1) we verify that $a_{n1} = a_{n2}$ .This implies that, using (A.2.3), that $\psi_{n1} = a_{n1}[u_{n1} + u_{n2}]$. Adjusting the coefficient a_{n1} in order to normalize ψ_{n1} we get

$$\psi_{n1} = [u_{n1} + u_{n2}]/\sqrt{2}$$

(A.3.3).

Substituting $\mathbb{C}_n^{(2)}$ given by (A.3.2) in the second equation (A.3.1) and using the same procedure adopted above we can show that

$$\psi_{n2} = [u_{n1} - u_{n2}]/\sqrt{2}$$

(A.3.4).

(A.4) *4−fold degeneracy hydrogen−like non−relativistic atom*

The first excited state n = 2, in the non−relativistic approximation, is *4−fold degenerate* represented[9−12] by the state functions $\{u_i\}_{i=1...4} = \{|210>, |210>, |211> , |21{-}1>\}$. To determine the shifts levels in the first−order perturbation theory we must consider a linear combination of the degenerate states,

$$\Psi = \sum_{j=1,...4} b_i\, u_i \qquad\qquad\qquad (A.4.1),$$

where u_i obey satisfies the unperturbed equation $H_o u_i = E_2 u_i$. Substituting into $(H_o + v)\, \Psi = 0$ we find the set of equations (see case b).

$$\sum_{j=1,2} (\, v_{ik} - \varepsilon\, \delta_{ik})\, b_i = 0 \qquad (k=1,2) \qquad\qquad (A.4.2),$$

where $\varepsilon = \mathcal{C} - E_2$ and $v_{ik} = <u_i|v|u_k>$. The matrix elements $v_{11}=v_{22} = 0$. The non−vanishing matrix elements are (see Section 1.1), putting, for instance, $v = eEz$:

$$v_{12} = v_{21} = -eE <200|\, z\, |210> = -3eEa_o \qquad\qquad (A.4.3).$$

The correction ε to the energy levels follows from the condition that the set of equations (A.4.2) be soluble. This condition reduces to the equation

$$(\varepsilon^2 - 9e^2 E^2 a_o^2)\, \varepsilon^2 = 0 \qquad\qquad (A.4.4).$$

The four roots of (A.4.4) are respectively, equal to

$$\varepsilon_1 = 3eEa_o\ (m = 0),\ \varepsilon_2 = -3eEa_o\ (m = 0)\ \text{and}\ \varepsilon_3 = \varepsilon_4 = 0\ (m = \pm 1) \quad (A.4.5)$$

Thus, when the external electric field E is switched on, the 4−fold degenerate level $n = 2$ is split into three levels. The states with $m = \pm 1$ are two−fold degenerate due to the z−symmetry of the problem.

(A.5) *2−fold degeneracy hydrogen−like relativistic atom.*

As seen in Section (1.2) the relativistic non−perturbed energy hydrogen−like atom eigenfunctions $|n\ell jm>$ are given by $u_- = \Psi_{n\,\ell\,j=\ell+1/2\,m}$ and $u_+ = \Psi_{n\,\ell\,j=\ell-1/2\,m}$ (see (1.2.4)). As explained in (4.3) the excited states $n \geq 2$ present effectively only a 2−fold degeneracy[15] with respect to the states with ℓ and $\ell\pm 1$ in the Stark effect context. Putting $u_1 = u_-$ and $u_2 = u_+$ and using the 2−level approach (A.3) with $v = -eEz$, $v_{11} = -eE < u_-|\, z\, |u_> = v_{22} = -eE < u_+|\, z\, |u_+> = 0$ and $v_{12} = -eE < u_-|\, z\, |u_+> = v_{21}$ we get, according to (A.3.2)

$$\mathcal{C}_n^{(1)} = E_n + v_{11} + v_{12} = E_n + eE < u_-|\, z\, |u_+>$$

and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (A.5.1).$

$$\mathcal{C}_n^{(2)} = E_n + v_{11} - v_{12} = E_n - eE < u_+|\, z\, |u_->$$

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