Rayleigh-Schrödinger Perturbation Theory

Introduction

Consider some physical system for which we had already solved the Schrödinger Equation completely but then wished to perform another calculation on the same physical system which has been slightly modified in some way. Could this be done without solving the Schrödinger Equation again? This would be particularly irksome if for example all we wanted to do was to subject the system (which we now feel is well described by the wave functions and energies) to a series of small changes such as imposing a series of electric or magnetic fields of various strengths.

Suppose the original system were described by the hamiltonian H_0, so that we had a complete set of energy eigenvalues and eigenfunctions labelled by (0):

$$H_0\psi_1^{(0)} = E_1^{(0)}\psi_1^{(0)}$$

$$H_0\psi_2^{(0)} = E_2^{(0)}\psi_2^{(0)} \tag{1}$$

$$H_0\psi_3^{(0)} = E_3^{(0)}\psi_3^{(0)}$$
$$\vdots$$

The modification of the system is described by the addition of a term V to the original hamiltonian so that the new hamiltonian is $H = H_0 + V$ and has solutions with unsuperscripted symbols

$$H\psi_1 = E_1\psi_1 \text{ ,}$$

$$H\psi_2 = E_2\psi_2 \quad \text{etc.}$$

Perturbation theory is based on the principle expressed in McLaurin and Taylor series that if a variable x is altered by a small amount λ then a function $f(x + \lambda)$ of the variable can be expressed as a power series in λ. Truncation of the series at the terms of different powers, $\lambda^0, \lambda^1, \lambda^2, \ldots$ defines the order of the perturbation as zeroth, first, second order etc. So the hamiltonian H and the general solution (ψ_i, E_i) for the perturbed system are written as

$$H = H_0 + \lambda V \tag{2}$$

and the Schrödinger equation for the perturbed system is

$$H\psi_i \equiv (H_0 + \lambda V)\psi_i = E_i\psi_i \qquad (3)$$

where

$$\psi_i = \psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \dots$$

and

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots$$

$\psi_i^{(1)}, \psi_i^{(2)}, \psi_i^{(3)}, \dots$ are the 1st-order, 2nd-order, 3rd-order corrections to the ith state wave functions; $E_i^{(1)}, E_i^{(2)}, E_i^{(3)}, \dots$ are the 1st-order, 2nd-order, 3rd-order corrections to the ith state energies.

Substituting for ψ_i and E_i back into the Schrödinger equation (3) we have

$$(H_0 + \lambda V)(\psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \dots)$$
$$= (E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots)(\psi_i^{(0)} + \lambda\psi_i^{(1)} + \lambda^2\psi_i^{(2)} + \dots)$$

$$H_0\psi_i^{(0)} + \lambda(V\psi_i^{(0)} + H_0\psi_i^{(1)}) + \lambda^2(H_0\psi_i^{(2)} + E_i^{(0)}\psi_i^{(2)}) + \dots =$$
$$E^{(0)}\psi_i^{(0)} + \lambda(E^{(0)}\psi_i^{(1)} + E^{(1)}\psi_i^{(0)}) + \lambda^2\left[\left(E_i^{(1)} - V\right)\psi_i^{(1)} + E_i^{(2)}\psi_i^{(0)}\right] + \dots \qquad (4)$$

which on equating the same powers of λ gives the equations

$$H_0\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)}$$
λ^0 zeroth order (same as eqns. 1)

$$V\psi_i^{(0)} + H_0\psi_i^{(1)} = E_i^{(1)}\psi_i^{(0)} + E_i^{(0)}\psi_i^{(1)}$$
λ^1 first order

$$(H_0 - E_i^{(0)})\psi_i^{(1)} = (E_i^{(1)} - V)\psi_i^{(0)}$$
λ^1 first order $\qquad (5)$

$$(H_0 - E_i^{(0)})\psi_i^{(2)} = (E_i^{(1)} - V)\psi_i^{(1)} + E_i^{(2)}\psi_i^{(0)}$$
λ^2 second order $\qquad (6)$

and we could go on . . .

The zeroth order equation tells us nothing new – it's just (1). But (5) and (6) define the conditions of first and second order perturbation theory, which come next.

1. First order perturbation

(a) Energies

For this we need eq. (5). We know the sets { $\psi_i^{(0)}$} and {$E_i^{(0)}$} but not the first-order corrections like { $\psi_i^{(1)}$} so let's express the latter as a combination of our basis set – the

complete zeroth order set of functions $\{\psi_i^{(0)}\}$:

$$\psi_i^{(1)} = \sum_{j(\neq i)} a_j \psi_j^{(0)}$$

(7)

Since $\psi_i^{(1)}$ is a *correction* to $\{\psi_i^{(0)}\}$ the summation excludes $j = i$. Substituting (7) in (5) we get

$$\sum_{j(\neq i)}' a_j (H_0 - E_i^0) \psi_j^{(0)} = (E_i^{(1)} - V) \psi_i^{(0)}$$

and since, from (1), $H_0 \psi_j^{(0)} = E_j^{(0)} \psi_j^{(0)}$ the operator H_0 in the last equation may be replaced by $E_j^{(0)}$ giving

$$\sum_j' a_j (E_j^{(0)} - E_i^0) \psi_j^{(0)} = (E_i^{(1)} - V) \psi_i^{(0)}$$

Multiply by $\psi_k^{(0)*}$ and integrate:

$$\sum_j' a_j (E_j^{(0)} - E_i^0) \underbrace{\int \psi_k^{(0)*} \psi_j^{(0)} d\tau}_{\delta_{kj}} = E_i^{(1)} \underbrace{\int \psi_k^{(0)*} \psi_i^{(0)} d\tau}_{\delta_{ki}} - \int \psi_k^{(0)*} V \psi_i^{(0)} d\tau$$

The integral on the LHS is the Kronecker delta δ_{kj} which means that it is *unity* if $k = j$ (normalisation) and *zero* otherwise (orthogonality). Its effect in the summation is to kill all the terms for which $j \neq k$, leaving

$$a_k (E_k^{(0)} - E_i^{(0)}) = E_i^{(1)} \delta_{ki} - <k|V|i>$$

(8)

where $<k|V|i>$ is a concise way of writing the integral $\int \psi_k^{(0)*} V \psi_i d\tau$.

In (7) put $i = k$. This gives our first useful result:

$$E_i^{(1)} = <i|V|i>$$

(9)

In other words, the first order correction to the *i*th energy is the expectation value $\int \psi_i^{(0)*} V \psi_i^{(0)} d\tau$ of V obtained using the zeroth order wave function $\psi_i^{(0)}$. None of the other functions $\psi_{j\neq i}^{(0)}$ are involved. So the energy corrected to first order is just

$$\boxed{E_i = E_i^{(0)} + \langle i|V|i \rangle}$$

(10)

(b) Wave functions

Next, try putting $i \neq k$ in (7). This provides the coefficient:

$$a_k = -\frac{\langle k|V|i\rangle}{E_k^{(0)} - E_i^{(0)}}$$

(11)

But this is what we need in (6) to express the first-order correction to the ith state wave function. So the wave function of the ith state, corrected to first order, is

$$\boxed{\psi_i = \psi_i^{(0)} - \sum_{k(\neq i)} \frac{\langle k|V|i\rangle}{E_k^{(0)} - E_i^{(0)}} \psi_k^{(0)}}$$

(12)

Unlike the theory leading to the first-order *energy* E_i in eqn. (9), in order to express the *wave function* to first order the functions and energies $\psi_{j\neq i}^{(0)}$ and $E_{j\neq i}^{(0)}$ of all the other zeroth-order states are involved. The function in eqn. (7) is then normalised after calculating all the coefficients expressed by eqn. (11).

2. Second order perturbation

To second order the wave function ψ_i and the energy E_i of the ith state are

$$\psi_i = \psi_i^{(0)} + \psi_i^{(1)} + \psi_i^{(2)}$$

and

$$E_i = E_i^{(0)} + E_i^{(1)} + E_i^{(2)}$$

As was done to express the 1st order corrections $\psi_i^{(1)}$ to the wave functions in (7), we also write the 2nd order corrections $\psi_i^{(2)}$ to the functions as a linear combination of the zero$^{\text{th}}$ order set $\{\psi_i^{(0)}\}$:

$$\psi_i^{(2)} = \sum_{j(\neq i)} b_j \psi_j^{(0)}$$

(13)

and substitute this expression in (6):

$$\sum_{j(\neq i)} b_j (H_0 - E_i^{(0)}) \psi_j^{(0)} = (E_i^{(1)} - V)\psi_i^{(1)} + E_i^{(2)}\psi_i^{(0)}$$

As before we use eq. (1)'s $H_0\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)}$ to replace H_0 by $E_j^{(0)}$, getting

$$\sum_{j(\neq i)} b_j (E_j^{(0)} - E_i^{(0)}) \psi_j^{(0)} = E_i^{(1)}\psi_i^{(1)} - V\psi_i^{(1)} + E_i^{(2)}\psi_i^{(0)}$$

Multiply by $\psi_k^{(0)}*$ and integrate:

$$\sum_{j(\neq i)} b_j (E_j^{(0)} - E_i^{(0)}) \int \psi_k^{(0)} {}^* \psi_j^{(0)} d\tau = E_i^{(1)} \int \psi_k^{(0)} {}^* \psi_i^{(1)} d\tau \underbrace{}_{\delta_{kj}} - \int \psi_k^{(0)} {}^* V \psi_i^{(1)} d\tau + E_i^{(2)} \int \psi_k^{(0)} {}^* \psi_i^{(0)} d\tau \underbrace{}_{\delta_{ki}}$$

(Note the Kronecker deltas! The one on the LHS limits the summation to a single term:

$$b_k (E_k^{(0)} - E_i^{(0)}) = E_i^{(1)} \int \psi_k^{(0)} {}^* \psi_i^{(1)} d\tau - \int \psi_k^{(0)} {}^* V \psi_i^{(1)} d\tau + E_i^{(2)} \delta_{ki} \qquad (14)$$

Opting for $k = i$ which we'll call i, not only does the LHS in (14) become zero but so also does the first term on the RHS because (7) expressed $\psi_i^{(1)}$ in terms of all the $\psi_j^{(1)}$ except $\psi_i^{(0)}$ — the first RHS term is a δ_{ki} where $k \neq i$ and is therefore zero. So we are left with

$$E_i^{(2)} = \int \psi_i^{(0)} {}^* V \psi_i^{(1)} d\tau$$

in which $\psi_i^{(1)}$ can be substituted from (12), giving

$$E_i^{(2)} = \sum_{k(\neq i)} \frac{\langle i|V|k\rangle \langle k|V|i\rangle}{E_i^{(0)} - E_k^{(0)}} \qquad (15)$$

and so the perturbed energy level E_i to second order is given by

$$\boxed{E_i = E_i^{(0)} + \langle i|V|i\rangle + \sum_{k(\neq i)} \frac{\langle i|V|k\rangle \langle k|V|i\rangle}{E_i^{(0)} - E_k^{(0)}}} \qquad (16)$$

The 2nd order correction to the wave function, $\psi_i^{(2)}$, could be calculated in a similar way to that in which we got $\psi_i^{(1)}$ that led to (11). This time it would be by opting for $k \neq i$ in (14), but we don't do this here.

3rd order perturbation

Here is the energy to 3rd order:

$$E_i = E_i^{(0)} + \langle i|V|i\rangle + \sum_{k(\neq i)} \frac{\langle i|V|k\rangle \langle k|V|i\rangle}{E_i^{(0)} - E_k^{(0)}} + \sum_{m\neq i} \sum_{n\neq i} \frac{\langle i|V|m\rangle \langle m|V|n\rangle \langle n|V|i\rangle}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)})} \qquad (16a)$$

0th order   1st order correction   2nd order correction   3rd order correction

If you look at how the 3rd order term is an extension of the 2nd order term you can guess how to write any higher order terms. The qth order correction to the energy would be

$$E_i^{(q)} = \sum_{m \neq i} \sum_{n \neq i} \cdots \sum_{p \neq i} \frac{\langle i|V|m\rangle \langle m|V|n\rangle \cdots \langle p|V|i\rangle}{(E_i^{(0)} - E_m^{(0)})(E_i^{(0)} - E_n^{(0)}) \cdots (E_i^{(0)} - E_p^{(0)})} \tag{17}$$

Some points concerning Rayleigh-Schrödinger Pertubation Theory

1. Although we stopped at second order, provided you were persistent enough there would be no restriction to proceeding to as high an order of perturbation as you wished, using the equations developed in the earlier part of this account. The energy interval ΔE_{ik} in the denominators of the correction terms (10, (16) or (17) show that successively higher order perturbations make successively smaller contributions.

2. All the rth-order corrections to the wave functions, $\psi_i^{(r)}$, and energies $E_i^{(r)}$, involve matrix elements $<k|V|i>$ of the perturbation operator V as in (15) in the numerator and energy differences $E_i^{(r)} - E_k^{(r)}$ in the denominator, with the sole exception of $E_i^{(1)}$ in (9). Physically this means that the procedure consists of *mixing in* functions into $\psi_i^{(0)}$, particularly from the set of high-energy unoccupied states $\psi_k^{(0)}$.

3. Because of the latter point, RS perturbation theory cannot be used if the state $\psi_k^{(0)}$ to be mixed with $\psi_i^{(0)}$ is energetically degenerate to this state.

4. From the perturbation corrections like those in eqns. (15) and (16) the mixing in of higher-order states makes the denominator negative. The effect is therefore to *stabilize* the lower-energy states.

5. Suppose that we were investigating the states of a molecule **A** that was influenced by another molecule **B** at a distance R from it. Then the perturbation operator V would consist of those terms describing the coulomb attractions and repulsions of the particles of **A** with those of **B**. The basis set of functions would be the complete set $\{\psi_i^{(0)}\}$ of functions for both molecules.

The expression for the perturbed energy states would start off like (16) but would explore the various orders until the higher-order terms become negligible. When the successive terms $E_i^{(1)}$, $E_i^{(2)}$, $E_i^{(3)}$, ... are examined they are found to be of the forms R^{-1}, R^{-2}, R^{-4}, R^{-6}, R^{-8}, ... which can be interpreted as the mutual interactions of the net charge, dipoles, quadrupoles, octupoles, ... (both permanent and induced) that are created on the two molecules. This result is sometimes interpreted in terms of the non-bonded London or van der Waals forces arising from the fluctuating electronic charges on the molecules **A** and **B**. While this description is a useful one, you don't need to think of fluctuating electronic charges — 'intermolecular forces' are the result of extending or 'perturbing' the hamiltonian of one molecule by the effect of the other. The effect would also be described by a single calculation using a hamiltonian for the two-molecule system.

Applications of Perturbation Theory

1. The electronic energy of the helium atom

The helium atom Hamiltonian is

$$H = \left(-\frac{\hbar^2}{2m}\nabla(1)^2 - \frac{\hbar^2}{2m}\nabla(2)^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

i.e $\quad H = \qquad\qquad\qquad H^0 \qquad\qquad\qquad\qquad\qquad + \quad V$

We shall treat the electronic repulsion term as a perturbation V of the 0th order Hamiltonian H^0, so

$$V = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \tag{18}$$

Zeroth order

Ignoring the electron-repulsion term (18) we express H^0 as a sum of the two remaining parts – one for each of the electrons (1) and (2)

$$H^0 = H^0(1) + H^0(2)$$

where
$$H^0(1) = -\frac{\hbar^2}{2m}\nabla(1)^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1}$$

and
$$H^0(2) = -\frac{\hbar^2}{2m}\nabla(2)^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$

These components $H^0(1)$ and $H^0(2)$ are each Hamiltonians for He$^+$ which is a 'hydrogen-like' atom, whose Schrödinger equations are exactly soluble:

$$H^0(1)\psi^{(0)}(1) = \varepsilon\,\psi^{(0)}(1)$$
$$H^0(2)\psi^{(0)}(2) = \varepsilon\,\psi^{(0)}(2)$$

Remember – we know $\psi^{(0)}$ and ε exactly. The ground state is described by the hydrogenic 1s atomic orbitals

$$\psi^{(0)} = N\exp(-Zr_1/a_0) \tag{19}$$

$$\varepsilon = -\frac{Z^2 m e^4}{2(4\pi\varepsilon_0\hbar)^2} \quad \text{(energy of 'the H-like atom')}$$

We write the complete 0$^{\text{th}}$ order Hamiltonian H^0 as $H^0(1,2)$ as a reminder that it involves the coordinates of both electrons and express the required 2-electron wave function $\psi^{(0)}(1,2)$ as the simple product

$$\psi^{(0)}(1,2) = \psi^{(0)}(1)\,\psi^{(0)}(2)$$

Operating on it with $H^0(1,2)$ we have

$$H^0(1,2)\,\psi^{(0)}(1,2) = [H^0(1) + H^0(2)]\,\psi^{(0)}(1)\,\psi^{(0)}(2)$$
$$= H^0(1)\,\psi^{(0)}(1)\,\psi^{(0)}(2) + H^0(2)\,\psi^{(0)}(1)\,\psi^{(0)}(2)$$

In the first term on the right hand side $H^0(1)$ operates on $\psi^{(0)}(1)$ giving $\varepsilon\,\psi^{(0)}(1)$ and leaving $\psi^{(0)}(2)$ unchanged. Similarly in the second term $H^0(2)$ operates on $\psi^{(0)}(2)$ giving $\varepsilon\,\psi^{(0)}(2)$ and leaving $\psi^{(0)}(1)$ unchanged, so we have

$$H^0(1,2)\,\psi^{(0)}(1,2) = \varepsilon\psi^{(0)}(1)\,\psi^{(0)}(2) + \varepsilon\psi^{(0)}(1)\,\psi^{(0)}(2)$$
$$= 2\varepsilon\psi^{(0)}(1)\,\psi^{(0)}(2)$$

So the eigenvalue equation

$$H^0(1,2)\,\psi^{(0)}(1,2) = 2\varepsilon\psi^{(0)}(1,2)$$

tells us that the He atom 0th order energy is 2ε, i.e. twice the energy of the He$^+$ ion. This is -54.4 eV so that the 0th order energy is

$$E^{(0)} = -108.8 \text{ eV}$$

This is physically meaningful because each of the two electrons is described as if it were in a He$^+$ atom, whose energy is ε. The term $\dfrac{e^2}{4\pi\varepsilon_0 r_{12}}$ that accounts for their mutual repulsion has been omitted to form H^0. But the energy is far too negative: the fact that the actual ground-state electronic energy of He is -79.0 eV (the sum of the first two ionization energies) shows that it is essential to include the interelectronic repulsion term in the Hamiltonian.

First order

From eq. (9) the first order correction to the energy is $E_{1s}^{(1)} = <1s|V|1s>$

$$E^{(1)} = \frac{e^2}{4\pi\varepsilon_0}\int\int \psi^{(0)}(1,2)*\frac{1}{r_{12}}\psi^{(0)}(1,2)d\tau(1)d\tau(2)$$

Substituting for $\psi^{(0)}$ from (19) and performing the integration leads to

$$E^{(1)} = 34.0 \text{ eV}.$$

This brings the energy of helium to first order to

$$E = E^{(0)} + E^{(1)}$$

$$= -108.8 + 34.0 = -74.8 \text{ eV} \qquad\qquad [\text{exptl. value } -79.0 \text{ eV}]$$

Second order

In order to form the matrix elements $\langle k|V|i\rangle \equiv \int \psi_k^{(0)*}V\psi_i^{(0)}d\tau$ required for substitution in eq. (15) we need all the 0th-order functions for $\psi^{(0)}$, i.e.

$$\psi_{1s}^{(0)}, \psi_{2s}^{(0)}, \psi_{2p_1}^{(0)}, \ldots$$

and all the corresponding 0th order energies

$$E_{1s}^{(0)}, E_{2s}^{(0)}, E_{2p_1}^{(0)}, \ldots$$

But these are known exactly since they are the solutions of a hydrogen-like atom. Evaluation of $E^{(2)}$ from eqs. (15) and (18) gives −4.3 eV, so the energy of helium to second order is

$$E = E^{(0)} + E^{(1)} + E^{(2)}$$
$$= -108.8 + 34.0 - 4.3 = -79.1 \text{ eV} \qquad \text{[exptl. value } -79.0 \text{ eV]}$$

Higher orders

The mixing of the higher order states $\psi_k^{(0)}$ into the ground state $\psi_{1s}^{(0)}$ should also include the continuum, i.e. states with energies greater than zero (which is the maximum energy obtained from the Bohr formula $\varepsilon_n = -\dfrac{Z^2 m e^4}{2\hbar^2 \varepsilon_0^2 n^2}$). The developm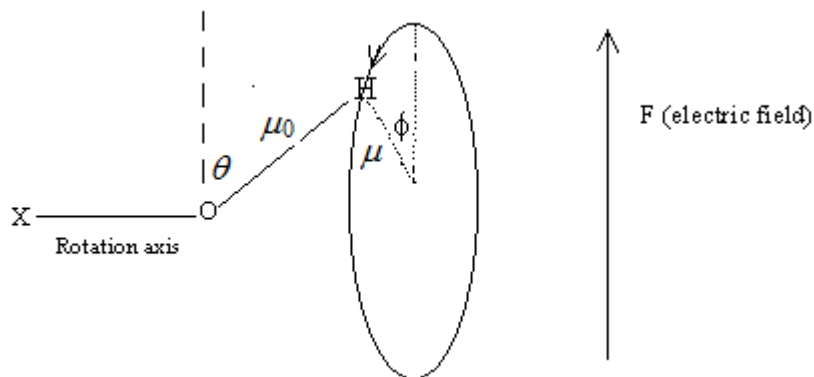ent of Nth order perturbation theory is tedious but routine, as is the numerical calculation of all the required matrix elements.

Calculations have been performed up to 13th order giving

$$E = -2.90372433 \text{ hartree (atomic units of energy)}$$
$$= -79.0161 \text{ eV}$$

(Exptl. value −79.0 eV)

2. Stark effect 1: The shifting of the torsional energy levels of an O—H group by an electric field.

Consider a part X—O—H of a molecule in which the O—H group rotates around the X—O bond. O—H has an electric dipole moment whose component in the plane perpendicular to the X—O bond (rotation axis) is μ. (If μ_0 is the dipole moment along O-H then $\mu = \mu_0 \cos \theta$) When an electric field $\mathbf{F}$ is applied in this plane (i.e. perpendicular to the rotation axis), μ rotates (in the xy plane) through azimuthal angles monitored as ϕ so that μ successively comes into and out of alignment with $\mathbf{F}$. The coupling of the dipole with the field produces an energy

$$V(\phi) = -\boldsymbol{\mu} \cdot \mathbf{F} = -\mu \ F \ \cos \phi$$

which is an energy perturbation term to the hamiltonian H^0 and μ is the component of the OH bond dipole moment perpendicular to the rotation axis. The total hamiltonian is

$$H = H^0 + V.$$

In the absence of an electric field ($\mathbf{F} = 0$) the solution of the Schrödinger Equation describing the internal rotation,

$$H^0 \psi^{(0)} = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \psi^{(0)} = E \psi^{(0)}$$

is the familiar one of a particle confined to a circle:

$$\psi_m^{(0)} = \sqrt{\tfrac{1}{2\pi}} e^{im\phi}$$

$$E_m^{(0)} = \frac{m^2 \hbar^2}{2I}$$

where $|m| = 0, \pm 1, \pm 2, \ldots$

We shall explore the perturbation of the torsional energy levels to second order by calculating the matrix elements of V that are required in the expression from eqn. (15):

$$E_m = \frac{m^2 \hbar^2}{2I} + \langle m|V|m \rangle + \sum_{m'(\neq m)} \frac{\langle m|V|m' \rangle \langle m'|V|m \rangle}{E_m^{(0)} - E_{m'}^{(0)}} \tag{20}$$

Both first- and second-order perturbation terms on the right of this equation require the matrix elements $V_{mm'}$ where $V_{mm'} = <m|V|m'>$ where $m = m'$ for the first-order and $m \neq m'$ for the second-order terms. We shall first evaluate the general matrix element $V_{mm'}$.

Substituting for

$$V = -\mu \ F \ \cos \phi = -\mu \ F \ \tfrac{1}{2}(e^{i\phi} + e^{-i\phi})$$

and the zeroth order functions

$$|m\rangle \equiv \sqrt{\frac{1}{2\pi}} e^{im\phi}$$

the matrix element $V_{mm'} \equiv \langle m|V|m' \rangle$ becomes

$$V_{mm'} = -\frac{1}{2\pi} \mu F \int_0^{2\pi} e^{-im\phi} \cos \phi e^{im'\phi} d\phi = -\frac{\mu F}{4\pi} \int_0^{2\pi} e^{-im\phi} (e^{i\phi} + e^{-i\phi}) e^{im'\phi} d\phi$$

$$= -\frac{\mu F}{4\pi} \left[\int_0^{2\pi} e^{i(m'-m+1)\phi} d\phi + \int_0^{2\pi} e^{i(m'-m-1)\phi} d\phi \right]$$

Both integrals are of the form $\int_0^{2\pi} e^{in\phi} d\phi$ where n is an integer. Now such an integral is zero unless $n = 0$, in which case it is 2π (see footnote[1]). Then as $m' = m \pm 1$ either of the two integrals contributes 2π and we have

$$V_{mn'} = -\tfrac{1}{2} \mu F \tag{20}$$

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[1]If $n \neq 0$, $\displaystyle\int_0^{2\pi} e^{in\phi} d\phi = \frac{1}{in} \left[e^{in\phi} \right]_0^{2\pi} = \frac{1}{in} \left[\cos 2n\phi + i \sin 2n\phi \right]_0^{2\pi} = \frac{1}{in} \left[1 + 0 - 1 \right] = 0$

Otherwise ($n = 0$), $\displaystyle\int_0^{2\pi} d\phi = 2\pi$

This is our required non-zero matrix element of perturbation V. <u>Note that as $V_{mm} = 0$ there is no first order correction to the energy</u>.

We can now calculate the second order perturbation term of the energy.

$$E_0^{(2)} = \frac{\langle 0|V|1\rangle\langle 1|V|0\rangle}{E_0^{(0)} - E_1^{(0)}} + \frac{\langle 0|V|-1\rangle\langle -1|V|0\rangle}{E_0^{(0)} - E_{-1}^{(0)}}$$

$$E_m = \frac{m^2\hbar^2}{2I} - \frac{\mu^2 F^2 I}{h^2} \quad .$$

$$E_0 = 0 - \frac{\mu^2 F^2 I}{2h^2}$$

Rotational level $m = 0$ of the rotor is therefore lowered by a quantity proportional to the square of the field intensity and of the dipole moment of the O—H bond. The 2-fold degeneracies of the levels are not lifted. (But they are when higher-order perturbation theory is applied!). Recall that μ is the component of the OH bond dipole moment perpendicular to the rotation axis, and we should write

What if the field were applied in a direction other than perpendicular to the torsional axis? Then $V = -\mathbf{\mu}\cdot\mathbf{F}$ would have components V_z and V_x from the couplings along and perpendicular to the this axis. The shift from V_x would be of the same form as the one we just calculated (but smaller because $\mathbf{F}$ has a smaller component in the circle around which the dipole moment is rotating), and V_z would be $-\mu F \cos\theta$ where θ is the (constant) angle between $\mathbf{\mu}$ and $\mathbf{F}$.

If the electric field were applied *parallel* to the rotational axis, ϕ would still go from 0 to 2π but as it rotated, the OH bond dipole would make a constant angle with the field. The energy shift would then be simply $-\mu F \sin\theta$ where $\mu \sin\theta$ is the angle made by the bond dipole with the torsional axis (and the electric field).

3. Stark effect 2: Degenerate perturbation theory.
Energy splittings in the H atom

We perturb the 0th order hamiltonian H^0 of the H atom by adding to it a term

$$V = eFz$$

Since z is antisymmetric (or odd) any diagonal matrix element V_{mm} is zero i.e. $\int_{-\infty}^{+\infty} \psi_m^* z \psi_m dz = 0$.

For this reason there is no Stark effect to 1st order PT.

In order to go to higher order we must form off-diagonal matrix elements V_{mn}. These elements will couple the $1s$ ground state $\psi_{1s}^{(0)}$ to higher states such as $\psi_{2s}^{(0)}$, $\psi_{2p_{+1}}^{(0)}$, $\psi_{2p_0}^{(0)}$, $\psi_{2p_{-1}}^{(0)}$ which will result in a *shifted* energy level of what was the *1s* ground state, but since this state is non-degenerate there will be no Stark *splitting*.

We therefore make the problem more interesting by replacing the ground state by the $n = 2$ state spanned by the four functions $2s$, $2p_{+1}$, $2p_0$, $2p_{-1}$. We should like to know to what extent this 4-fold degeneracy is removed by the Stark effect.

Zeroth order functions

The four basis functions of the $n = 2$ shell of the H atom, and their energies (all equal, $E_{n=2}$) are known exactly. The functions can be written as products of functions involving spherical coordinates r, θ, φ in the form $R(r) \times \Theta(\theta) \times \Phi(\phi)$, and the only factor of these which will concern us will be $\Phi(\varphi)$ which is of the form $e^{im\phi}$ where $m = 0$ for 2s and 1, 0, −1 respectively for $2p_{+1}$, $2p_0$, $2p_{-1}$. Written this way these functions are obviously eigenfunctions of the angular momentum operator $\ell_z = \dfrac{\hbar}{i} \dfrac{\partial}{\partial \varphi}$ with eigenvalues $m\hbar$.

s	$\psi(2s) = \chi_{2s} e^{i0\phi}$	$\ell_z \psi(2s)$	$= 0\hbar\ \psi(2s)$
p_{+1}	$\psi(2p_{+1}) = \chi_{2p} e^{i\phi}$	$\ell_z \psi(2p_{+1})$	$= +1\hbar\ \psi(2p_{+1})$
p_0	$\psi(2p_0) = \chi_{2p} e^{i0\phi}$	$\ell_z \psi(2p_0)$	$= 0\hbar\ \psi(2p_0)$
p_{-1}	$\psi(2p_{-1}) = \chi_{2p} e^{-i\phi}$	$\ell_z \psi(2p_{-1})$	$= -1\hbar\ \psi(2p_{-1})$

where χ_{2s} and χ_{2p} are the parts of the 2s and 2p AO functions without the $\Phi(\phi)$ factor.

The reason that these functions are eigenfunctions of ℓ_z is because this operator commutes with the hamiltonian. But as ℓ_z also commutes with the perturbation term $V = e\mathcal{E}z$, matrix elements $V_{mm'}$ formed from functions functions ψ_m and $\psi_{m'}$ corresponding to different angular momenta $m\hbar$ and $m'\hbar$ are zero,

i.e. $\boxed{\text{if} \qquad <i|\ell_z|j> = 0 \qquad \text{then} \qquad <i|V|j> = 0 \qquad \text{also.}}$

This is because, as ℓ_z is a hermitian operator its eigenfunctions are orthogonal if they belong to different eigenvalues, i.e. matrix elements $<m|\ell_z|m'> = 0$. The only non-zero elements of V are for basis functions corresponding to the same eigenvalue of ℓ_z. However, for the same reason as in the application of perturbation theory of a Stark electric field to a molecular torsion, diagonal matrix elements of V are zero because the perturbation $V = eFz$, is not totally symmetric, i.e. $<m|V|m> = 0$ for all $|m>$.

So we have the following.

(a) All diagonal elements of V are zero

(b) Non-zero elements of V must be from pairs of functions corresponding to the same eigenvalue of ℓ_z.

This leaves only one pair of functions that forms a non-zero element with V: that between $2s$ and $2p_0$. Since their degeneracy does not allow them to be used in perturbation theory we shall need to calculate the eigenvalues of the energy matrix of **V** spanned by the four basis functions

$$(s, \; p_{+1}, \; p_0, \; p_{-1})$$

All the elements of **V** will be zero except two, those formed by ($2s$ and $2p_0$), and by ($2p_0$ and $2s$). The zeroth order energy $E^{(0)}$ is the energy of the $2s$ and $2p$ orbitals (all four have the same energy, because for all hydrogen-like atoms with one electron, a subshell with principal quantum number n is n^2-fold degenerate. The perturbation energy matrix **V** is therefore

$$\mathbf{V} = \begin{bmatrix} 0 & \langle s|V|p_0 \rangle & 0 & 0 \\ \langle p_0|V|s \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

The complete hamiltonian matrix, $\mathbf{H} = \mathbf{H^0} + \mathbf{V}$ is therefore

$$\mathbf{H} = \begin{pmatrix} E_2^{(0)} & 0 & 0 & 0 \\ 0 & E_2^{(0)} & 0 & 0 \\ 0 & 0 & E_2^{(0)} & 0 \\ 0 & 0 & 0 & E_2^{(0)} \end{pmatrix} + \begin{pmatrix} 0 & v & 0 & 0 \\ v & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} E_2^{(0)} & v & 0 & 0 \\ v & E_2^{(0)} & 0 & 0 \\ 0 & 0 & E_2^{(0)} & 0 \\ 0 & 0 & 0 & E_2^{(0)} \end{pmatrix}$$

where $E_2^{(0)}$ is the energy of the $n = 2$ shell (recall that for a hydrogen atom $E_{2s}^{(0)} = E_{2p}^{(0)}$) and the perturbation matrix element $<i|V|j>$ is assigned to a parameter v

i.e. $$v = eF\langle 2s|z|2p_z\rangle \tag{19}$$

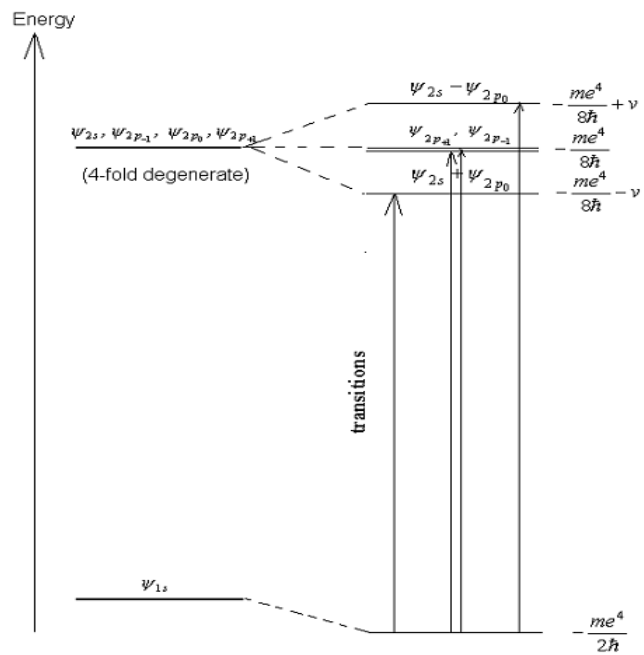that is proportional to the electric field F. $\mathbf{H}$ is 'block-diagonal', the blocks being (2×2), (1×1) and (1×1). The energy eigenvalues are obtained in the standard way by setting the determinant of each block equal to zero:

$$\begin{vmatrix} E_2^{(0)} - E & v & 0 & 0 \\ v & E_2^{(0)} - E & 0 & 0 \\ 0 & 0 & E_2^{(0)} - E & 0 \\ 0 & 0 & 0 & E_2^{(0)} - E \end{vmatrix} \equiv (E_2^{(0)} - E)^2 \begin{vmatrix} E_2^{(0)} - E & v \\ v & E_2^{(0)} - E \end{vmatrix} = 0$$

i.e. $$(E_2^{(0)} - E)^2 [(E_2^{(0)} - E)^2 - v^2] = 0$$

So the four energy eigenvalues are $E = E_2^{(0)}, E_2^{(0)}, E_2^{(0)} + v, E_2^{(0)} - v$. The block diagonal form of the energy matrix tells us immediately that two of the eigenvalues are zero. In other words, of the 4 degenerate states $2s$, $2p_{+1}$, $2p_0$, $2p_{-1}$ two of them ($2p_{+1}$ and $2p_{-1}$) are unaffected by the electric field and so remain doubly degenerate. The degeneracy of the two remaining levels is removed as the $2s$ and $2p_0$ states combine to produce two new states whose energies are raised and lowered by an amount v.

Energy

$\psi_{2s} - \psi_{2p_0}$ $\quad -\dfrac{me^4}{8\hbar} + \nu$

$\psi_{2s},\ \psi_{2p_{-1}},\ \psi_{2p_0},\ \psi_{2p_{+1}}$

$\psi_{2p_{+1}},\ \psi_{2p_{-1}}$ $\quad -\dfrac{me^4}{8\hbar}$

(4-fold degenerate)

$\psi_{2s} + \psi_{2p_0}$ $\quad -\dfrac{me^4}{8\hbar} - \nu$

transitions

ψ_{1s}

$-\dfrac{me^4}{2\hbar}$

Unperturbed atom

$\mathbf{H}^0$

Atom perturbed by
an electric field F

$\mathbf{H}^0 + e\,Fz$