Time independent perturbation (20)

The major task in any practical application of quantum mechanics is to solve the eigenvalue equation of the Hamiltonian H of the system. Considering the bound states, the eigenvalues of H are discrete and corresponding to each eigenvalue there may be one or several linearly independent eigenvectors. The eigenvalue equation, i.e., the time-independent Schrödinger equation is

$$H|E_n\rangle = E_n|E_n\rangle \quad \text{- - - - - (1)}$$

Except for few special cases the eigenvalue equation cannot be solved exactly. The equation then has to be solved numerically, or approximate methods have to be devised to solve the equation to any desired order of accuracy.

Time independent perturbation theory applies when H is of the form

$$H = H_0 + V \quad \cdots \quad (2)$$

where the eigenvalues and eigenvectors of H_0 are completely known and V is an additional time-independent potential called the perturbation.

Let us denote the eigenvalues of H_0 as $E_n^{(0)}$ and the corresponding eigenvectors as $|E_n^{(0)}\rangle$ so that the eigenvalue equation for H_0 is written as

$$H|E_n^{(0)}\rangle = E_n^{(0)}|E_n^{(0)}\rangle \quad \cdots \quad (3)$$

We assume that all the eigenvalues and the eigenvectors of H_0 are already calculated.

Non-degenerate perturbation theory

We assume that the eigenvalues $E_n^{(0)}$ of H_0 are non-degenerate, i.e., there is only one linearly independent eigenvector $|E_n^{(0)}\rangle$ corresponding to $E_n^{(0)}$. Since the eigenvectors $|E_n^{(0)}\rangle$ form a complete set of vectors, we can express any vector in the Hilbert space as a linear combination of the eigenvectors of H_0. Further, eigenvectors belonging to different eigenvalues are orthogonal. We also normalize each of the eigenvectors of H_0. So these eigenvectors form a complete orthonormal set, i.e.,

$$\langle E_n^{(0)} | E_m^{(0)} \rangle = \delta_{nm} \quad \text{- - - - (4)}$$

and

$$\hat{1} = \sum_k |E_k^{(0)}\rangle \langle E_k^{(0)}| \quad \text{- - - - [5]}$$

Now we modify the eigenvalue equation for the full Hamiltonian H (Eq. (1)) as

$$(H_0 + \lambda V)|E_n\rangle_\lambda = E_{n\lambda}|E_n\rangle_\lambda \quad \cdots (6)$$

where we have introduced a real parameter λ whose value lies in the range (0, 1). The eigenvalue $E_{n\lambda}$ and the eigenvector $|E_n\rangle_\lambda$ in Eq. (6) are not quite the same as the corresponding quantities in Eq. (1). It is only in the limit $\lambda \to 1$ would $E_{n\lambda}$ and $|E_n\rangle_\lambda$ in Eq. (6) coincide with actual values. Furthermore, ~~consideration to be taken~~,

$$\lim_{\lambda \to 0} E_{n\lambda} = E_n^{(0)}$$

$$\lim_{\lambda \to 0} |E_n\rangle_\lambda = |E_n^{(0)}\rangle .$$

Thus, as $\lambda \to 0$, the perturbation is switched off and as $\lambda \to 1$, the full perturbation V is operative.

We will now set up a perturbative scheme for solving $E_{n,\lambda}$ and $|E_n\rangle_\lambda$ and at the end set $\lambda = 1$. First, we write $E_{n,\lambda}$ and $|E_n\rangle_\lambda$ as power series in λ:

$$E_{n\lambda} = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \quad (7)$$

$$|E_n\rangle_\lambda = |E_n^{(0)}\rangle + \lambda |E_n^{(1)}\rangle + \lambda^2 |E_n^{(2)}\rangle + \cdots \quad (8)$$

Substituting Eqs. (7) and (8) in Eq. (6) we have

$$(H_0 + \lambda V)(|E_m^{(0)}\rangle + \lambda |E_n^{(1)}\rangle + \lambda^2 |E_n^{(2)}\rangle + \cdots)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots)(|E_n^{(0)}\rangle + \lambda |E_n^{(1)}\rangle + \lambda^2 |E_n^{(2)}\rangle + \cdots$$

or

$$H_0 |E_n^{(0)}\rangle + \lambda (H_0 |E_n^{(1)}\rangle + V |E_n^{(0)}\rangle) + \lambda^2 (H_0 |E_n^{(2)}\rangle + V |E_n^{(1)}\rangle)$$

$$+ \cdots$$

$$= E_n^{(0)} |E_n^{(0)}\rangle + \lambda (E_n^{(0)} |E_n^{(1)}\rangle + E_n^{(1)} |E_n^{(0)}\rangle)$$

$$+ \lambda^2 (E_n^{(0)} |E_n^{(2)}\rangle + E_n^{(1)} |E_n^{(1)}\rangle + E_n^{(2)} |E_n^{(0)}\rangle)$$

We will solve this equation order by order in λ. So we equate the coefficients of equal powers of λ on both sides of the above equation. We have up to order λ^2

λ^0 $$H_0 |E_n^{(0)}\rangle = E_n^{(0)} |E_n^{(0)}\rangle \quad (8)$$

λ $$H_0 |E_n^{(1)}\rangle + V|E_n^{(0)}\rangle = E_n^{(0)} |E_n^{(1)}\rangle + E_n^{(1)} |E_n^{(0)}\rangle \quad (9)$$

λ^2 $$H_0 |E_n^{(2)}\rangle + V|E_n^{(1)}\rangle = E_n^{(0)} |E_n^{(2)}\rangle + E_n^{(1)} |E_n^{(1)}\rangle + E_n^{(2)} |E_n^{(0)}\rangle . \quad (10)$$

Eq. (8) is considered solved because we have assumed that we ~~can~~ know fully the eigenvalues and eigenvectors of H_0.

First-order correction to energy : $E_n^{(1)}$

The first order correction to the unperturbed energy of the n^{th} level is $E_n^{(1)}$. This can be found from Eq. (9). We start by taking the product of Eq. (9) with $\langle E_n^{(0)}|$. We get

$$\langle E_n^{(0)} | H_0 | E_n^{(1)} \rangle + \langle E_n^{(0)} | V | E_n^{(0)} \rangle$$

$$= E_n^{(0)} \langle E_n^{(0)} | E_n^{(1)} \rangle + E_n^{(1)} \langle E_n^{(0)} | E_n^{(0)} \rangle \quad (11)$$

Now

$$H_0 | E_n^{(0)} \rangle = E_n^{(0)} | E_n^{(0)} \rangle$$

since H_0 is hermitian

$$\langle E_n^{(0)} | H_0 = E_n^{(0)} \langle E_n^{(0)} | .$$

Also $$\langle E_n^{(0)} | E_n^{(0)} \rangle = 1 .$$

Therefore, Eq. (11) becomes

$$E_n^{(0)} \cancel{\langle E_n^{(0)} | E_n^{(1)} \rangle} + \langle E_n^{(0)} | V | E_n^{(0)} \rangle$$

$$= E_n^{(0)} \cancel{\langle E_n^{(0)} | E_n^{(1)} \rangle} + E_n^{(1)} .$$

or $$\boxed{E_n^{(1)} = \langle E_n^{(0)} | V | E_n^{(0)} \rangle \equiv V_{nn}} \quad \cdots (12)$$

This is a fundamental result of time independent perturbation theory of non-degenerate levels. The first order correction to the n^{th} energy level is the expectation value of the perturbation potential in the unperturbed state.

First-order correction to the eigenstate.

The ket $|E_n^{(1)}\rangle$ is the first-order correction to the zeroth-order eigenket $|E_n^{(0)}\rangle$. The ket $|E_n^{(1)}\rangle$ is also found from Eq. (9). First we write $|E_n^{(1)}\rangle$ as

$$|E_n^{(1)}\rangle = \sum_m |E_m^{(0)}\rangle\langle E_m^{(0)}|E_n^{(1)}\rangle \quad \cdots (13)$$

or

$$|E_n^{(1)}\rangle = \sum_m |E_m^{(0)}\rangle C_{mn}^{(1)} \quad \cdots (14)$$

where we have defined

$$C_{mn}^{(1)} = \langle E_m^{(0)}|E_n^{(1)}\rangle \quad \cdots (15).$$

Using Eq. (14) we write Eq. (9) as

$$\sum_m H_0|E_m^{(0)}\rangle C_{mn}^{(1)} + V|E_n^{(0)}\rangle = \sum_m E_n|E_m^{(0)}\rangle C_{mn}^{(1)} + E_n^{(1)}|E_n^{(0)}\rangle$$

N,

$$\sum_m \left(E_n^{(0)} - E_m^{(0)}\right) |E_m^{(0)}\rangle C_{mn}^{(1)} = V|E_n^{(0)}\rangle - E_n^{(1)} |E_n^{(0)}\rangle$$

Taking the scalar product with $\langle E_k^{(0)}|$ we have

$$\left(E_n^{(0)} - E_k^{(0)}\right) C_{kn}^{(1)} = \langle E_k^{0} | V | E_n^{(0)}\rangle - E_n^{(1)} \delta_{kn} \quad \ldots (16)$$

If $k = n$, the left side is zero and we recover the result

$$E_n^{(1)} = \langle E_n^{(0)} | V | E_n^{(0)}\rangle .$$

Thus, we cannot determine $C_{nn}^{(1)}$ from Eq. (16).

This coefficient has to be determined from considerations of normalization of the eigenvectors as discussed later.

Next, if $k \neq n$, Then Eq. (16) becomes

$$\left(E_n^{(0)} - E_k^{(0)}\right) C_{kn}^{(1)} = \langle E_k^{(0)} | V | E_n^{(0)}\rangle , \quad k \neq n$$

or

$$\boxed{C_{kn}^{(1)} = \frac{\langle E_k^{(0)} | V | E_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} \quad (k \neq n) . \quad \ldots (17)}$$

Using Eqs (14) and (17) the first order correction to the state is

$$|E_n^{(1)}\rangle = \sum_k |E_k^{(0)}\rangle C_{kn}^{(1)}$$

or

$$|E_n^{(1)}\rangle = C_{nn}^{(1)} |E_n^{(0)}\rangle + \sum_{\substack{k \\ k \neq n}} \frac{\langle E_k^{(0)} | V | E_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |E_k^{(0)}\rangle \quad \text{---(18)}$$

Writing

$$V_{kn} \equiv \langle E_k^{(0)} | V | E_n^{(0)} \rangle$$

we have

$$\boxed{|E_n^{(1)}\rangle = C_{nn}^{(1)} |E_n^{(0)}\rangle + \sum_{\substack{k \\ k \neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})} |E_k^{(0)}\rangle} \quad \text{---(19)}$$

Therefore, up to first order in λ, the eigenstate $|E_n\rangle_\lambda$ is (see Eq. (8))

$$|E_n\rangle_\lambda = |E_n^{(0)}\rangle + \lambda |E_n^{(1)}\rangle + O(\lambda^2)$$

i.e.,

$$|E_n\rangle_\lambda = |E_n^{(0)}\rangle + \lambda c_{nn}^{(1)} |E_n^{(0)}\rangle + \lambda \sum_{\substack{k \\ k \neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})} |E_k^{(0)}\rangle + O(\lambda^2) \quad \cdots (20)$$

We want to normalize $|E_n\rangle_\lambda$. Up to first order

$$\underset{\lambda}{\langle} E_n | E_n \rangle_\lambda = 1 + O(\lambda^2)$$

Using Eq (20), the normalization condition can be written as (noting λ is real)

$$1 + \lambda c_{nn}^{(1)} + \lambda c_{nn}^{(1)*} + O(\lambda^2) = 1 + O(\lambda^2)$$

or $$c_{nn}^{(1)} + c_{nn}^{(1)*} = 0$$

i.e., $$\text{Re}\, c_{nn}^{(1)} = 0 .$$

Thus $c_{nn}^{(1)}$ is a purely imaginary number. We write $$c_{nn}^{(1)} = i\alpha \quad (\alpha = \text{real}).$$

Hence Eq. (20) can be written as

$$|E_n\rangle_\lambda = (1+i\lambda\alpha)\,|E_n^{(0)}\rangle + \lambda \sum_{\substack{k \\ k\neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})}\,|E_k^{(0)}\rangle + O(\lambda^2)$$

or

$$|E_n\rangle_\lambda = e^{i\lambda\alpha}\,|E_n^{(0)}\rangle + \lambda \sum_{\substack{k \\ k\neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})}\,|E_k^{(0)}\rangle + O(\lambda^2)$$

or

$$e^{-i\lambda\alpha}\,|E_n\rangle_\lambda = |E_n^{(0)}\rangle + \lambda \sum_{\substack{k \\ k\neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})}\,|E_k^{(0)}\rangle + O(\lambda^2)$$

Now $e^{-i\lambda\alpha}$ is an overall phase factor which does not effect the normalization of $|E_n\rangle_\lambda$ up to first order. This factor can be set equal to 1 without loss of generality. So we take $\alpha = 0$, i.e.,

$$\langle E_n^{(0)} | E_n^{(1)} \rangle \equiv c_{nn}^{(1)} = i\alpha = 0$$

i.e., we can choose $|E_n^{(1)}\rangle$ to be orthogonal to $|E_n^{(0)}\rangle$.

Thus, up to first order

$$|E_n\rangle_\lambda = |E_n^{(0)}\rangle + \lambda \sum_{\substack{k \\ k \neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})} |E_k^{(0)}\rangle$$

Setting $\lambda = 1$ we get the desired eigenket of the full Hamiltonian H up to first order in the perturbing potential, i.e.,

$$|E_n\rangle = |E_n^{(0)}\rangle + \underbrace{\sum_{\substack{k \\ k \neq n}} \frac{V_{kn}}{(E_n^{(0)} - E_k^{(0)})} |E_k^{(0)}\rangle}_{|E_n^{(1)}\rangle} \quad (21)$$

Second-order correction to energy: $E_n^{(2)}$

We can find the second order correction to the energy, i.e., $E_n^{(2)}$ from Eq. (10). First, multiply Eq. (10) by $\langle E_n^{(0)}|$. We get

$$\langle E_n^{(0)}|H_0|E_n^{(2)}\rangle + \langle E_n^{(0)}|V|E_n^{(1)}\rangle$$

$$= E_n^{(0)}\langle E_n^{(0)}|E_n^{(2)}\rangle + E_n^{(1)}\langle E_n^{(0)}|E_n^{(1)}\rangle + E_n^{(2)}. \quad (22)$$

Since

$$\langle E_n^{(0)}|H_0 = E_n^{(0)}\langle E_n^{(0)}|$$

the first term on the left hand side of Eq. (22) cancels the first term on the right. Therefore, we have

$$\langle E_n^{(0)}|V|E_n^{(1)}\rangle = E_n^{(1)}\langle E_n^{(0)}|E_n^{(1)}\rangle + E_n^{(2)}$$

i.e.,

$$E_n^{(2)} = \langle E_n^{(0)}|V|E_n^{(1)}\rangle - E_n^{(1)}\langle E_n^{(0)}|E_n^{(1)}\rangle \quad (23).$$

Writing

$$|E_n^{(1)}\rangle = \sum_m |E_m^{(0)}\rangle\langle E_m^{(0)}|E_n^{(1)}\rangle$$

we have

$$E_n^{(2)} = \sum_m \langle E_n^{(0)}|V|E_m^{(0)}\rangle\langle E_m^{(0)}|E_n^{(1)}\rangle - E_n^{(1)}\langle E_n^{(0)}|E_n^{(1)}\rangle$$

We now isolate the term with $m = n$ in the summation,

$\therefore$ We have

$$E_n^{(2)} = \langle E_n^{(0)}|V|E_n^{(0)}\rangle\langle E_n^{(0)}|E_n^{(1)}\rangle + \sum_{\substack{m \\ m\neq n}} \langle E_n^{(0)}|V|E_m^{(0)}\rangle\langle E_m^{(0)}|E_n^{(1)}\rangle$$

$$- E_n^{(1)}\langle E_n^{(0)}|E_n^{(1)}\rangle \qquad (24)$$

But

$$\langle E_n^{(0)}|V|E_n^{(0)}\rangle = E_n^{(1)}.$$

So the first term cancels the third term in Eq (3).

We then have

$$E_n^{(2)} = \sum_m{}' \langle E_n^{(0)}|V|E_m^{(0)}\rangle\langle E_m^{(0)}|E_n^{(1)}\rangle. \quad \cdots\cdots (25)$$

where the prime on the summation symbol means that the term $m = n$ is excluded from the sum.

Now, we have found previously (Eq. 17)

$$\langle E_m^{(0)} | E_n^{(1)} \rangle \equiv C_{mn}^{(1)} = \frac{\langle E_m^{(0)} | V | E_n^{(0)} \rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

Substituting this in Eq. (25) we have

$$E_n^{(2)} = \sum_m{}' \frac{\langle E_n^{(0)} | V | E_m^{(0)} \rangle \langle E_m^{(0)} | V | E_n^{(0)} \rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \quad (26)$$

This is the final expression for the second order correction $E_n^{(2)}$ for the n^{Th} level.

Next, introducing the notation

$$V_{nm} \equiv \langle E_n^{(0)} | V | E_m^{(0)} \rangle$$

we can write Eq. (26) as

$$E_n^{(2)} = \sum_m{}' \frac{V_{nm} V_{mn}}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

Since V is a hermitian operator

$$V_{mn} = V_{nm}^{*},$$

so,

$$\boxed{E_n^{(2)} = \sum_m{}' \frac{|V_{nm}|^2}{(E_n^{(0)} - E_m^{(0)})}.} \qquad (27)$$

Note that the second order correction to the ground state energy is negative. Also, in the second order, the effect of an energy level above the n^{th} level is to push down the energy of the n^{th} level. The effect of a level below the n^{th} level is to push up the energy of the n^{th} level. It is as if, the levels are repelling each other in the 2nd order of perturbation.

Time independent perturbation theory (degenerate states).

In perturbation theory we seek a solution of the eigenvalue equation of the Hamiltonian H, where

$$H = H_0 + H' , \quad - - - - - - - - (1)$$

We assume that the eigenvalues and eigenfunctions of the unperturbed Hamiltonian H_0 are known. We then ask how the energy and the wave function of the n^{th} level of H_0 are modified when the perturbation H' is turned on.

Suppose that the n^{th} level of H_0 is g_n-fold degenerate. Therefore

$$H_0 \psi^{(0)}_{n\alpha} = E^{(0)}_n \psi^{(0)}_{n\alpha} \; ; \; \alpha = 1, 2, \cdots g_n . \quad - - (2)$$

The g_n wave functions $\left\{ \psi^{(0)}_{n\alpha} ; \alpha = 1, 2, \cdots g_n \right\}$ are linearly independent of each other and they are all orthogonal to the unperturbed wave functions belonging to ~~different~~ other energy levels.

~~Although they need not be orthogonal among themselves,~~

We note that any linear combination of the vectors $\{\psi^{(0)}_{n\alpha}\,;\,\alpha=1,\cdots g_n\}$ is also an eigenvector of H_0 with the same eigenvalue $E^{(0)}_n$. Thus if we construct a vector $\chi^{(0)}_{n\beta}$ as

$$\chi^{(0)}_{n\beta} = \sum_{\alpha=1}^{g_n} C_{\alpha\beta}\,\psi^{(0)}_{n\alpha} \qquad \cdots\cdots (3)$$

then $\chi^{(0)}_{n\beta}$ is also an eigenvector of H_0 with eigenvalue $E^{(0)}_n$:

$$H\chi^{(0)}_{n\beta} = E^{(0)}_n \chi^{(0)}_{n\beta}\,. \qquad \cdots\cdots (4)$$

Now the vectors $\{\psi^{(0)}_{n\alpha}, \alpha=1,2,\cdots g_n\}$ need not be orthonormal. However, by using the the Schmidt procedure, we can make the degenerate eigenvectors orthonormal by taking suitable linear combinations if they are not orthonormal to start with. This procedure can be applied to all vectors belonging to every level.

Thus, we will assume that all vectors whether belonging to the same level or not are normalized and orthogonal to each other, i.e.,

$$\langle \psi^{(0)}_{n\alpha} | \psi^{(0)}_{m\beta} \rangle = \delta_{nm}\delta_{\alpha\beta} . \quad \text{- - - - - (5)}$$

Further, the eigenvectors of H_0 span the entire Hilbert space, i.e., they form a complete set of states. The completeness condition can be written as

$$\hat{1} = \sum_k \sum_{\alpha=1}^{g_k} | \psi^{(0)}_{k\alpha} \rangle \langle \psi^{(0)}_{k\alpha} | . \qquad (6)$$

The "full" eigenvalue equation for the n^{th} level is written as

$$H \psi_{n\alpha} = E_{n\alpha} \psi_{n\alpha} \; ; \; \alpha = 1, 2, \cdots g_n , \qquad (7)$$

In order to facilitate counting of different orders, we may write

$$H = H_0 + \lambda H'$$

where λ is a real parameter which we set

equal to one at the end of our calculations. The eigenvalues $E_{n\alpha}$ and the eigenvector $\psi_{n\alpha}$ are now functions of λ. In the limit $\lambda \to 0$ $E_{n\alpha}$ tends to $E_n^{(0)}$, i.e.,

$$\lim_{\lambda \to 0} E_{n\alpha} = E_n^{(0)}, \tag{8}$$

However, there is a difficulty in taking the corresponding limits for $\psi_{n\alpha}$. Since there are g_n linearly independent unperturbed eigenfunctions corresponding to $E_n^{(0)}$, we do not know to which particular eigenfunction will $\psi_{n\alpha}$ tend to when $\lambda \to 0$. Suppose

$$\psi_{n\alpha} \xrightarrow[\lambda=0]{} \chi_{n\alpha}^{(0)}$$

where $\chi_{n\alpha}^{(0)}$ is some linear combination of $\{\psi_{n\alpha}^{(0)}, \alpha = 1, 2, \cdots g_n\}$.

Now we write

$$\psi_{n\alpha} = \chi^{(0)}_{n\alpha} + \lambda \psi^{(1)}_{n\alpha} + \lambda^2 \psi^{(2)}_{n\alpha} + \cdots \qquad (9)$$

where $\chi^{(0)}_{n\alpha}$ is as yet some undetermined linear combination of $\{\psi^{(0)}_{n\alpha}; \alpha = 1, 2, \cdots g_n\}$. We also write the perturbed energy $E_{n\alpha}$ as

$$E_{n\alpha} = E^{(0)}_n + \lambda E^{(1)}_{n\alpha} + \lambda^2 E^{(2)}_{n\alpha} + \cdots \qquad (10)$$

where we have used the fact that $E^{(0)}_{n\alpha} = E^{(0)}_n$ for all α.

Next, we substitute (9) and (10) in Eq. (7). We have

$$(H_0 + \lambda H') (\chi^{(0)}_{n\alpha} + \lambda \psi^{(1)}_{n\alpha} + \cdots)$$
$$= (E^{(0)}_n + \lambda E^{(1)}_{n\alpha} + \cdots)(\chi^{(0)}_{n\alpha} + \lambda \psi^{(1)}_{n\alpha} + \cdots).$$

Equating the coefficients of equal powers of λ on both sides of this equation we obtain in the zeroth order the equation

$$H_0 \chi^{(0)}_{n\alpha} = E^{(0)}_n \chi^{(0)}_{n\alpha}$$

which is Eq. (4) written earlier. In the first order

order we have

$$\left(H_0 - E_n^{(0)}\right)\psi_{n\alpha}^{(1)} = \left(E_{n\alpha}^{(1)} - H'\right)\chi_{n\alpha}^{(0)} \quad \ldots \quad (11)$$

Now, we write

$$\psi_{n\alpha}^{(1)} = \sum_{k\beta}{}' C_{k\beta,\,n\alpha}\,\psi_{k\beta}^{(0)} \quad \ldots\ldots\ldots \quad (12)$$

and

$$\chi_{n\alpha}^{(0)} = \sum_{\beta=1}^{g_n} a_{\beta\alpha}\,\psi_{n\beta}^{(0)} \quad \ldots\ldots\ldots \quad (13)$$

where the indices α and β refer explicitly to degeneracy.

Substituting (12) and (13) in Eq. (11) we find

$$\left(H_0 - E_n^{(0)}\right)\sum_{k\beta}{}' C_{k\beta,\,n\alpha}\,\psi_{k\beta}^{(0)} = \left(E_{n\alpha}^{(1)} - H'\right)\sum_{\beta=1}^{g_n} a_{\beta\alpha}\,\psi_{n\beta}^{(0)}$$

or $$\sum_{k,\beta}{}' C_{k\beta,\,n\alpha}\left(E_k^{(0)} - E_n^{(0)}\right)\psi_{k\beta}^{(0)} = \sum_{\beta=1}^{g_n} a_{\beta\alpha}\left(E_{n\alpha}^{(1)} - H'\right)\psi_{n\beta}^{(0)}$$

Taking the scalar product with $\psi_{m\gamma}^{(0)}$ and using the orthonormality $\langle \psi_{m\gamma}^{(0)} \mid \psi_{k\beta}^{(0)} \rangle = \delta_{mk}\,\delta_{\gamma\beta}$, we have

$$C_{m\gamma,n\alpha}\left(E_m^{(0)} - E_n^{(0)}\right)$$

$$= \sum_{\beta=1}^{g_n}{}' a_{\beta\alpha}\left(E_{n\alpha}^{(1)}\delta_{mn}\delta_{\gamma\beta} - H'_{m\gamma,n\beta}\right) \quad (14)$$

where we have written

$$H'_{m\gamma,n\beta} = \langle \psi_{m\gamma}^{(0)} | H' | \psi_{m\beta}^{(0)} \rangle \quad (15)$$

First order correction to energy

First, ~~let us~~ choose $m = n$ in Eq. (14). Then the left hand side of this equation is zero. We then have

$$\sum_{\beta=1}^{g_n}{}' \left(H'_{n\gamma,n\beta} - E_{n\alpha}^{(1)}\delta_{\gamma\beta}\right) a_{\beta\alpha} = 0 \quad (16)$$

Simplifying the notation by writing

$$H'_{n\gamma,n\beta} = H'^{(n)}_{\gamma\beta}$$

we write Eq. (16) as

$$\sum_{\beta=1}^{g_n} \left(H'^{(n)}_{\gamma\beta} - E^{(1)}_{n\alpha}\, \delta_{\gamma\beta} \right) a_{\beta\alpha} = 0 \quad \text{- - - - (17)}$$

Equation (16) is a set of g_n linear equations for the unknowns $\{a_{1\alpha}, a_{2\alpha}, \cdots a_{g_n\alpha}\}$ corresponding to $E^{(1)}_{n\alpha}$. The value of $E^{(1)}_{n\alpha}$ are not known a priori.

However, we note that, for a solution of Eq. (17) to exist, the determinant formed by the coefficients of $a_{\beta\alpha}$ must vanish, i.e.,

$$\therefore \det \left[H'^{(n)}_{\gamma\beta} - E^{(1)}_{n\alpha}\, \delta_{\gamma\beta} \right] = 0 \quad \text{- - - - (18)}$$

This is called the secular equation, which is a polynomial of degree g_n in $E^{(1)}_{n\alpha}$. It has g_n real roots $E^{(1)}_{n1}, E^{(1)}_{n2}, \cdots E^{(1)}_{n,g_n}$. If all these roots are distinct, the degeneracy is completely removed to first order in the

perturbation. On the other hand, if some or all roots of Eq. (18) are identical, the degeneracy is only partially (or not at all) removed. The residual degeneracy may then either be removed in higher order perturbation theory, or it may persist in all orders.

Next, substituting each of the roots $E_{n\alpha}^{(1)}$, $\alpha = 1, 2, \cdots g_n$, in Eq. (17) we can solve for the coefficients $a_{1\alpha}, a_{2\alpha}, \cdots a_{g_n\alpha}$.

In fact, one of the coefficients remain undetermined and the other coefficients are found in terms of the undetermined one. This is because the set of equations given by Eq. (17) are homogeneous. The undetermined coefficient is then obtained up to a phase by requiring that the eigenvector

$a_{\beta\alpha}$; $\beta = 1, 2, \cdots g_n$ be normalized to unity.

$$a^*_{1\alpha} a_{1\alpha} + a^*_{2\alpha} a_{2\alpha} + a^*_{3\alpha} a_{3\alpha} + \cdots + a^*_{g_n\alpha} a_{g_n\alpha} = 1$$

i.e $$\sum_{\beta=1}^{g_n} a^*_{\beta\alpha} a_{\beta\alpha} = 1 \; ; \quad \alpha = 1, 2, \cdots g_n$$

The correct zeroth order wave function is then found using Eq. (13), i.e.,

$$\chi^{(0)}_{n\alpha} = \sum_{\beta=1}^{g_n} a_{\beta\alpha} \psi^{(0)}_{n\beta} .$$

The functions $\chi^{(0)}_{n\alpha}$ are eigenvectors of H' in the eigen subspace of $E^{(0)}_n$ with eigenvalue $E^{(1)}_{n\alpha}$, i.e.,

$$H' \chi^{(0)}_{n\alpha} = E^{(1)}_{n\alpha} \chi^{(0)}_{n\alpha} \; ; \quad \alpha = 1, 2, \cdots g_n$$

and the coefficients $a_{\beta\alpha}$, $\beta = 1, 2, \cdots g_n$ form the g_n-component representation of the eigenvector $\chi^{(0)}_{n\alpha}$ using the basis $\{\psi^{(0)}_{n\beta}, \beta = 1, 2, \cdots g_n\}$.

Thus

$$\chi^{(0)}_{n\alpha} \doteq \begin{pmatrix} a_{1\alpha} \\ a_{2\alpha} \\ \vdots \\ a_{g_n\alpha} \end{pmatrix}.$$

Thus, in summary, the first-order corrections to the n^{th} degenerate level of H_0 with energy $E_n^{(0)}$ are obtained by diagonalizing H' in the ~~space~~ eigen subspace of $E_n^{(0)}$. The eigenvalues of H' are the corrections to the energy and the corresponding eigenvectors of H' are the zeroth order approximation of the wavefunction.

Once the correct zero-order wavefunctions $\chi^{(0)}_{n\alpha}$, $\alpha = 1, 2, \cdots g_n$, have been determined, the first order correction to $\psi^{(1)}_{n\alpha}$ to the wavefunction and second-order energy correction $E^{(2)}_{n\alpha}$ can be obtained in a way similar to non-degenerate perturbation theory.

Ex Calculate the first order energy shifts for the first three states of the infinite square well of width a in one dimension due to the perturbation

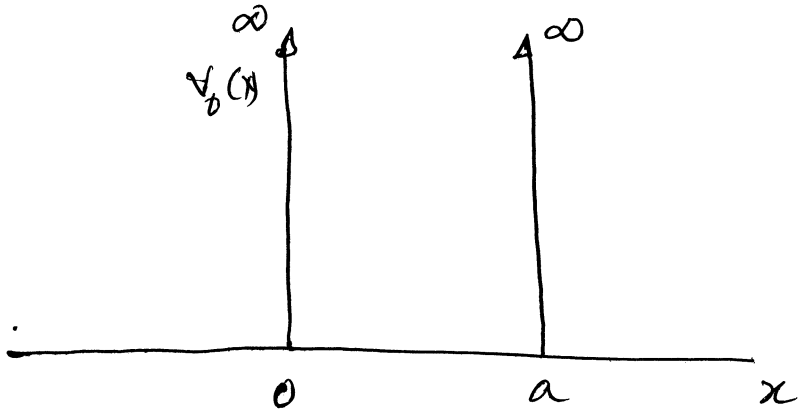
$$V(x) = V_0 \frac{x}{a}.$$

Ans $$H = H_0 + V$$

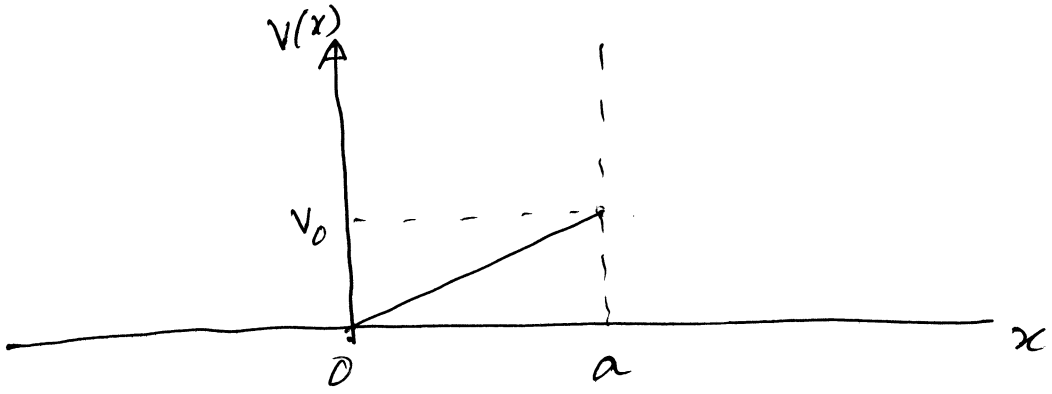
where $$H_0 = \frac{p^2}{2m} + V_0(x)$$

where

$$V_0(x) = \begin{cases} 0 & 0 \le x \le a \\ \infty & \text{otherwise} \end{cases}$$



The perturbing potential is shown below



Unperturbed states.

$$H_0 |E^{(0)}\rangle = E^{(0)} |E^{(0)}\rangle$$

In coordinate representation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(0)}(x)}{dx^2} + V(x)\psi^{(0)}(x) = E^{(0)}\psi^{(0)}(x)$$

In region $0 < x < a$, $V(x) = 0$. Therefore

$$-\frac{\hbar^2}{2m}\frac{d^2\psi^{(0)}(x)}{dx^2} = E^{(0)}\psi^{(0)}(x)$$

or

$$\frac{d^2\psi^{(0)}(x)}{dx^2} + k^2\psi^{(0)}(x) = 0 \qquad (0 < x < a) \quad \text{---} (1)$$

where $k = \sqrt{\frac{2mE_0}{\hbar^2}}$.

The wave function must be zero at the boundaries of the potential and outside the potential.

The general solution of the interior wave function $\psi^{(0)}(x)$ is

$$\psi^{(0)}(x) = A \sin kx + B \cos kx.$$

Since $\psi^{(0)}(x=0) = 0$, we must have $B = 0$. Thus

$$\psi^{(0)}(x) = A \sin kx.$$

Since $\psi^{(0)}(x=a)$ is also zero, we must also have

$$\sin ka = 0$$

or $$ka = \pi, 2\pi, 3\pi, \cdots$$

i.e $$ka = n\pi, \quad n = 1, 2, 3, \cdots \quad \cdots (2)$$

Eq. (2) is the quantization condition. The unperturbed energy levels are

$$E_n^{(0)} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{n^2\pi^2}{a^2}\right) = \frac{\pi^2\hbar^2}{2ma^2} n^2. \quad \cdots (3)$$

The first three energy levels are

$$E_1^{(0)} = \frac{\pi^2 \hbar^2}{2ma^2}$$

$$E_2^{(0)} = 4\,\frac{\pi^2 \hbar^2}{2ma^2}$$

$$E_3^{(0)} = 9\,\frac{\pi^2 \hbar^2}{2ma^2}.$$

Now we will normalize the unperturbed wave functions. For an arbitrary level n,

$$\psi_n^{(0)}(x) = A_n \sin k_n x$$

$$\therefore \int \psi_n^{(0)*}(x)\, \psi_n^{(0)}(x)\, dx = 1$$

$$\text{or} \quad |A_n|^2 \int \sin^2 k_n x \, dx = 1$$

$$\text{or} \quad |A_n|^2 \int_0^a \frac{1}{2}(1 - \cos 2k_n x) = 1$$

$$\text{or} \quad |A_n|^2 \cdot \frac{1}{2}\left[a - \underbrace{\int_0^a \cos 2k_n x \, dx}_{=0}\right] = 1$$

$$\text{or} \quad |A_n|^2 \frac{a}{2} = 1$$

Therefore we can choose

$$A_n = \sqrt{\frac{2}{a}}.$$

Therefore, normalized unperturbed wave functions for the first three levels are

$$\psi_1^{(0)}(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$

$$\psi_2^{(0)}(x) = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a}$$

$$\psi_3^{(0)}(x) = \sqrt{\frac{2}{a}} \sin \frac{3\pi x}{a}.$$

First order correction to energy.

The first-order energy corrections are then

$$E_1^{(1)} = \langle \psi_1^{(0)} | V | \psi_1^{(0)} \rangle = \frac{2}{a} \cdot \frac{V_0}{a} \int_0^a x \sin^2 \frac{\pi x}{a} dx = \frac{V_0}{2}$$

$$E_2^{(1)} = \langle \psi_2^{(0)} | V | \psi_2^{(0)} \rangle = \frac{2}{a} \cdot \frac{V_0}{a} \int_0^a x \sin^2 \frac{2\pi x}{a} dx = \frac{V_0}{2}$$

$$E_3^{(1)} = \langle \psi_3^{(0)} | V | \psi_3^{(0)} \rangle = \frac{2}{a} \cdot \frac{V_0}{a} \int_0^a x \sin^2 \frac{3\pi x}{a} dx = \frac{V_0}{2}$$

Therefore, to first order, the perturbed energies are

$$E_1 = E_1^{(0)} + E_1^{(1)} = \frac{\pi^2\hbar^2}{2ma^2} + \frac{V_0}{2}$$

$$E_2 = E_2^{(0)} + E_2^{(1)} = 4\frac{\pi^2\hbar^2}{2ma^2} + \frac{V_0}{2}$$

$$E_3 = E_3^{(0)} + E_3^{(1)} = 9\frac{\pi^2\hbar^2}{2ma^2} + \frac{V_0}{2}$$

Ex A particle of mass m moves in a 1-dimensional oscillator potential

$$V(x) = \frac{1}{2} m \omega^2 x^2 .$$

In the nonrelativistic limit, where the kinetic energy and momentum are related by

$$T = \frac{p^2}{2m} ,$$

the ground state energy is well-known to be $E_0 = \frac{1}{2}\hbar\omega$. Relativistically, the kinetic energy and the momentum are related by

$$T = E - mc^2 = \sqrt{m^2c^4 + p^2c^2} - mc^2 .$$

(a) Determine the lowest order correction to the kinetic energy due to relativistic effects.

(b) Considering the correction to the kinetic energy as a perturbation, compute the relativistic correction to the ground state energy.

Ans

(a) We have

$$T = E - mc^2 = \sqrt{m^2c^4 + p^2c^2} - mc^2$$

$$= mc^2 \sqrt{1 + \frac{p^2c^2}{m^2c^4}} - mc^2$$

$$\simeq mc^2 \left(1 + \frac{p^2c^2}{2m^2c^4} - \frac{p^4c^4}{8m^4c^8} + \cdots\right) - mc^2$$

$$= mc^2 \left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \cdots\right) - mc^2$$

$$= \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \cdots$$

$$\left((1+x)^n = 1 + nx + \frac{n(n-1)}{2!}x^2 + \cdots \right)$$

(b) The unperturbed Hamiltonian is

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2.$$

H_0 represents a one-dimensional harmonic oscillator.

The eigenstates and the eigenvalues are

$$H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$$

where $$E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots$$

We take the perturbation to be

$$V = -\frac{p^4}{8m^3c^2}.$$

The energy correction for the ground state is then

$$E_0^{(1)} = \langle 0|V|0\rangle$$

$|0\rangle$ = unperturbed ground state

$$= -\langle 0|\frac{p^4}{8m^3c^2}|0\rangle$$

$$E_0^{(1)} = -\frac{1}{8m^3c^2}\langle 0|p^4|0\rangle$$

where

$$p = ip_0(a^+ - a), \quad p_0 = \sqrt{\frac{\hbar m\omega}{2}}.$$

Thus

$$E_0^{(1)} = -\frac{1}{8m^3c^2}\,\frac{\hbar^2m^2\omega^2}{4}\langle 0|(a^+-a)^4|0\rangle$$

$$E_0^{(1)} = -\frac{\hbar^2\omega^2}{32mc^2}\langle 0|(a^+-a)^4|0\rangle$$

~~$E_0^{(1)} = -\frac{\hbar^2\omega^2}{32mc^2}\langle 0|(a^\dagger - a)(a^\dagger - a)(a^\dagger - a)|0\rangle$~~

$$E_0^{(1)} = -\frac{\hbar^2\omega^2}{32mc^2}\langle 0|(a^\dagger - a)(a^\dagger - a)(a^\dagger - a)(a^\dagger - a)|0\rangle$$

$$= +\frac{\hbar^2\omega^2}{32mc^2}\langle 0|a\,(a^\dagger - a)(a^\dagger - a)\,a^\dagger|0\rangle$$

$$= \frac{\hbar^2\omega^2}{32mc^2}\langle 1|\,(a^\dagger - a)(a^\dagger - a)\,|1\rangle$$

$$= \frac{\hbar^2\omega^2}{32mc^2}\langle 1|\,(a^\dagger - a)\left(\sqrt{2}\,|2\rangle - |0\rangle\right)$$

$$= \frac{\hbar^2\omega^2}{32mc^2}\langle 1|\left(\sqrt{6}\,|3\rangle - |1\rangle - 2\,|1\rangle\right)$$

$$= \frac{\hbar^2\omega^2}{32mc^2}\langle 1|\left(\sqrt{6}\,|3\rangle - 3\,|1\rangle\right)$$

$$= -\frac{3\hbar^2\omega^2}{32mc^2}. \quad (\text{Ans})$$

Note

$a|n\rangle = \sqrt{n}\,|n-1\rangle$

$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$

Ex Find the first order correction to the n^{th} level of a one-dimensional harmonic oscillator perturbed by the potential

$$H'(x) = \epsilon_3 x^3 + \epsilon_4 x^4.$$

Ans For an unperturbed one-dimensional harmonic oscillator, the Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2.$$

The eigenvalue equation H_0 is completely solved. We have

$$H_0|n\rangle = E_n|n\rangle$$

where

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \cdots.$$

Now the first-order correction to energy is

$$E_n^{(1)} = \langle n | H' | n \rangle$$

$$= \langle n | \epsilon_3 x^3 | n \rangle + \langle n | \epsilon_4 x^4 | n \rangle .$$

The expectation value of x^3 in any unperturbed state of the harmonic oscillator is zero, because the wave function corresponding to an unperturbed state is either even or odd. So

$$\langle n | x^3 | n \rangle = \int u_n^*(x)\, x^3\, u_n(x)\, dx = 0$$

because the integrand is odd. Therefore

$$E_n^{(1)} = \epsilon_4 \langle n | x^4 | n \rangle \qquad \text{- - - (1)}$$

At this stage, we can work out the expectation value of x^4 in the n^{th} unperturbed state, i.e., the right hand side of Eq. (1), by using the wave function of the n^{th} unperturbed state :

$$E_n^{(1)} = \epsilon_4 \langle n|x^4|n\rangle$$

$$= \epsilon_4 \int_{-\infty}^{\infty} u_n^*(x)\, x^4\, u_n(x)\, dx \,.$$

The wave function $u_n(x)$ involve the hermite polynomials $H_n(x)$ and the integration in the above equation is nontrivial. It is easier to find the expectation value $\langle n|x^4|n\rangle$ using the creation operator and the destruction operator, $a^\dagger$ and a.

We define

$$a = \frac{1}{\sqrt{2m\hbar\omega}} (m\omega x + ip)$$

$$a^\dagger = \frac{1}{\sqrt{2m\hbar\omega}} (m\omega x - ip) \,.$$

In terms of a and $a^\dagger$, the unperturbed Hamiltonian is

$$H_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 x^2 = \left(a^\dagger a + \frac{1}{2}\right)\hbar\omega \,.$$

We can write the operators $\hat{x}$ and $\hat{p}$ in terms of a and a^+ ;

$$\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(\hat{a}+\hat{a}^+)$$

$$\hat{p} = \frac{1}{i}\left(\frac{m\hbar\omega}{2}\right)^{1/2}(\hat{a}-\hat{a}^+).$$

We also have

$$a|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$a^+|n\rangle = \sqrt{n+1}\,|n+1\rangle .$$

The perturbing Hamilton is

$$H' = \epsilon_3 x^3 + \epsilon_4 x^4$$

i.e.,

$$H' = \epsilon_3\left(\frac{\hbar}{2m\omega}\right)^{3/2}(a+a^+)^3 + \epsilon_4\left(\frac{\hbar}{2m\omega}\right)^2(a+a^+)^4 .$$

The first order correction to energy is

$$E_n^{(1)} = \epsilon_3 \langle n|x^3|n\rangle + \epsilon_4 \langle n|x^4|n\rangle$$

The first term is zero, as we have argued previously. So

$$E_n^{(1)} = \epsilon_4 \langle n|x^4|n\rangle$$

$$E_n^{(1)} = \epsilon_4 \frac{\hbar^2}{4m^2\omega^2} \langle n|(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)(a+a^\dagger)|n\rangle$$

The expression on the right hand side has sixteen terms, each term having four factors a or $a^\dagger$ in a variety of different orders. Only terms containing two a's and two $a^\dagger$'s yield non-zero contributions. These terms are:

~~$E_n^{(1)} = \epsilon_4 \frac{\hbar^2}{4m^2\omega^2}$~~

$$E_n^{(1)} = \epsilon_4 \frac{\hbar^2}{4m^2\omega^2} \langle n | aaa^\dagger a^\dagger + aa^\dagger aa^\dagger + aa^\dagger a^\dagger a + a^\dagger aaa^\dagger + a^\dagger aa^\dagger a + a^\dagger a^\dagger aa | n \rangle$$

The six expectation values in the above expression can be calculated in a straight forward manner.

o)

$$\langle n | aaa^\dagger a^\dagger | n \rangle = \langle n | aaa^\dagger | n+1 \rangle \sqrt{n+1}$$
$$= \langle n | aa | n+2 \rangle \sqrt{n+2}\sqrt{n+1}$$
$$= \langle n | a | n+1 \rangle \sqrt{n+2}\sqrt{n+2}\sqrt{n+1}$$
$$= \underbrace{\langle n | n \rangle}_{=1} \sqrt{n+1}\sqrt{n+2}\sqrt{n+2}\sqrt{n+1}$$
$$= (n+1)(n+2).$$

$$\langle n | aa^\dagger aa^\dagger | n \rangle = \langle n | aa^\dagger a | n+1 \rangle \sqrt{n+1}$$
$$= \langle n | aa^\dagger | n \rangle \sqrt{n+1}\sqrt{n+1}$$
$$= \langle n | a | n+1 \rangle \sqrt{n+1}\sqrt{n+1}\sqrt{n+1}$$
$$= \langle n | n \rangle \sqrt{n+1}\sqrt{n+1}\sqrt{n+1}\sqrt{n+1}$$
$$= (n+1)^2$$

$$\langle n|aa^\dagger a^\dagger a|n\rangle = \langle n|aa^\dagger a^\dagger|n-1\rangle\sqrt{n}$$
$$= \langle n|aa^\dagger|n\rangle\sqrt{n}\sqrt{n}$$
$$= \langle n|a|n+1\rangle\sqrt{n+1}\sqrt{n}\sqrt{n}$$
$$= \langle n|n\rangle\sqrt{n+1}\sqrt{n+1}\sqrt{n}\sqrt{n}$$
$$= n(n+1)$$

$$\langle n|a^\dagger a\, aa^\dagger|n\rangle = n(n+1)$$

$$\langle n|a^\dagger a\, a^\dagger a|n\rangle = n^2$$

$$\langle n|a^\dagger a^\dagger aa|n\rangle = \langle n|a^\dagger a^\dagger a|n-1\rangle\sqrt{n}$$
$$= \langle n|a^\dagger a^\dagger|n-2\rangle\sqrt{n-1}\sqrt{n}$$
$$= \langle n|a^\dagger|n-1\rangle\sqrt{n-1}\sqrt{n-1}\sqrt{n}$$
$$= \langle n|n\rangle\sqrt{n}\sqrt{n-1}\sqrt{n-1}\sqrt{n}$$
$$= n(n-1)$$

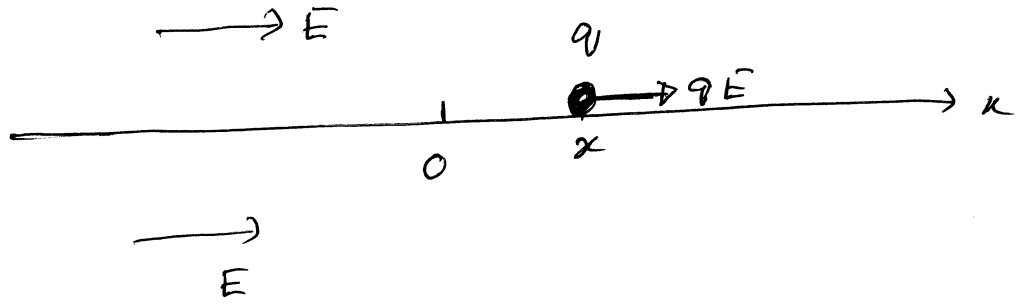
Putting everything together

$$E_n^{(1)} = \epsilon_4\frac{\hbar^2}{4m^2\omega^2}\Big[(n+1)(n+2)+(n+1)^2+n(n+1)$$
$$+n(n+1)+n^2+n(n-1)\Big]$$

$$\boxed{E_n^{(1)} = \frac{\epsilon_4\hbar^2}{4m^2\omega^2}(6n^2+6n+3)}$$

Ex Linear harmonic oscillator of charge $q = +e$ (e is positive) and mass m perturbed by a uniform ~~mag~~ electric field E in the x direction.

Ans.



$$V(x) = V(0) - qEx = -qEx \quad (\text{Assume } V(0) =$$

Thus,

$$V(x) = -qEx .$$

Here $V(x)$ is the electrical potential energy of the oscillator. We will take this as a perturbation.

The full Hamiltonian of the system is then

$$H = \underbrace{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2}_{H_0} \underbrace{- qEx}_{V}$$

The first order correction to the energy of the n^{th} level of the harmonic oscillator due to its interaction with the electric field is then

$$E_n^{(1)} = \langle n|V|n\rangle = -eE\langle n|x|n\rangle = 0$$

because the integrand is odd in the coordinate representation.

We now calculate the energy correction in the 2nd order.

$$E_n^{(2)} = \sum_{\substack{m \\ m \neq n}} \frac{|V_{mn}|^2}{(E_n^{(0)} - E_m^{(0)})}.$$

Here

$$V_{mn} = \langle m|V|n\rangle = -eE\langle m|x|n\rangle.$$

Therefore

$$E_n^{(2)} = -\sum_{\substack{m \\ m \neq n}}$$

Therefore

$$E_n^{(2)} = (-eE)^2 \sum_{\substack{m \\ m \neq n}} \frac{|\langle m|x|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

Next,

$$x = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a + a^+)$$

$$\therefore \quad \langle m|x|n\rangle = \left(\frac{\hbar}{2m\omega}\right)^{1/2} \langle m|a + a^+|n\rangle$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \left[\sqrt{n}\,\langle m|n-1\rangle + \sqrt{n+1}\,\langle m|n+1\rangle\right]$$

$$= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \left[\sqrt{n}\,\delta_{m\,n-1} + \sqrt{n+1}\,\delta_{m\,n+1}\right]$$

Hence

$$E_n^{(2)} = e^2 E^2 \sum_{\substack{m \\ m \neq n}} \frac{|\langle m|x|n\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$= e^2 E^2 \sum_{\substack{m \\ m \neq n}}$$

$$\text{or} \quad E_n^{(2)} = e^2E^2 \left[\frac{|\langle n-1|x|n\rangle|^2}{\left(E_n^{(0)} - E_{n-1}^{(0)}\right)} + \frac{|\langle n+1|x|n\rangle|^2}{\left(E_n^{(0)} - E_{n+1}^{(0)}\right)} \right]$$

$$= e^2E^2 \left[\frac{n}{\hbar\omega} + \frac{(n+1)}{-\hbar\omega} \right] \times \left(\frac{\hbar}{2m\omega}\right)$$

$$= -\frac{e^2E^2}{2m\omega^2}.$$

The correction to the energy of the n^{th} level up to second order is then

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

$$= \left(n+\tfrac{1}{2}\right)\hbar\omega + 0 + \left(-\frac{e^2E^2}{2m\omega^2}\right)$$

$$\boxed{E_n = \left(n+\tfrac{1}{2}\right)\hbar\omega - \frac{e^2E^2}{2m\omega^2}}$$

In the present situation the problem can be solved exactly merely by shifting the origin. This can be easily seen as follows:

$$H = H_0 + V = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 - eEx$$

$$= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2\left(x^2 - \frac{2eE}{m\omega^2}x\right)$$

Now, we can write $\left(x^2 - \frac{2eE}{m\omega^2}x\right)$ as follows:

$$x^2 - \frac{2eE}{m\omega^2}x = x^2 - 2\frac{eE}{m\omega^2}x + \left(\frac{eE}{m\omega^2}\right)^2 - \left(\frac{eE}{m\omega^2}\right)^2$$

$$= \left(x - \frac{eE}{m\omega}\right)^2 - \frac{e^2E^2}{m^2\omega^4}.$$

Therefore, the Hamiltonian H can be written as

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}m\omega^2\left(x - \frac{eE}{m\omega}\right)^2 - \frac{1}{2}m\omega^2 \cdot \frac{e^2E^2}{m^2\omega^4}$$

i.e.,

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}m\omega^2\left(x - \frac{eE}{m\omega}\right)^2 - \frac{e^2E^2}{2m\omega^2}$$

Let $\xi = x - \frac{eE}{m\omega^2}$

$$\therefore \quad H = -\frac{\hbar^2}{2m}\frac{d^2}{d\xi^2} + \frac{1}{2}m\omega^2\xi^2 - \frac{e^2E^2}{2m\omega^2}.$$

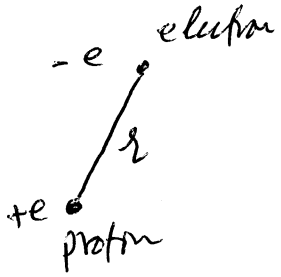
Thus, the exact eigenvalue spectrum is

$$E_n = \left(n+\tfrac{1}{2}\right)\hbar\omega - \frac{e^2E^2}{2m\omega^2}\,; \quad n = 0, 1, 2, \ldots .$$

In the present problem, the second order perturbation theory happens to give the correct result.

Ex Calculate the shift in energy of the 1s state (i.e., the ground state) of hydrogen if the proton is assumed to be a uniformly charged spherical shell of radius 10^{-15} m rather than a point charge. Use first-order perturbation theory.

Ans.

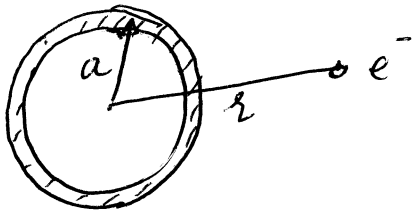


Unperturbed system: proton is a point charge.

The Hamiltonian of the unperturbed system is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 + V_0(r) = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

Perturbed system.



The Proton is a very thin shell of radius a. The value of a is 10^{-15} m.

The potential for the perturbed system is

$$V(r) = \begin{cases} -\dfrac{e^2}{4\pi\epsilon_0 r}, & r > a \\ -\dfrac{e^2}{4\pi\epsilon_0 a} & r < a \end{cases}$$

Therefore

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

$$= \begin{cases} -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{e^2}{4\pi\epsilon_0 a} & \text{for } r < a \\ -\dfrac{\hbar^2}{2m}\nabla^2 - \dfrac{e^2}{4\pi\epsilon_0 r} & \text{for } r > a. \end{cases}$$

The unperturbed Hamiltonian

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \text{for all } r.$$

Therefore, perturbation H' is

$$H' = H - H_0$$

$$= \begin{cases} -\dfrac{e^2}{4\pi\epsilon_0 a} + \dfrac{e^2}{4\pi\epsilon_0 r} & \text{for } r < a \\ 0 & \text{for } r > a. \end{cases}$$

Now, the ground state energy of the Hydrogen atom (taking the proton to be a point charge) is

$$E_0 = -\frac{e^2}{(4\pi\epsilon_0)2a_0} = -13.6\,eV$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = \text{Bohr radius} = 0.5\times10^{-10}\,m.$$

The ground state wavefunction is

$$\psi_{1s}^{(0)}(r) = \frac{2}{(4\pi)^{1/2}a_0^{3/2}}e^{-r/a_0}.$$

Hence the first-order correction is

$$E^{(1)} \equiv \Delta E = \langle \psi_{1s}^{(0)} | H' | \psi_{1s}^{(0)} \rangle$$

$$= \int \psi_{1s}^{(0)*}(1)\, H'\, \psi_{1s}(2)\, d^3r$$

$$= \frac{4}{(4\pi)a_0^3}\cdot 4\pi\int_0^a e^{-2r/a_0}\left(\frac{e^2}{4\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 a}\right)r^2\,dr$$

$$= \frac{4}{a_0^3}\cdot\frac{e^2}{(4\pi\epsilon_0)}\int_0^a e^{-2r/a_0}\left(\frac{1}{r}-\frac{1}{a}\right)r^2\,dr$$

Here $a = 10^{-15}\,m$

In the integral above

$$\left(\frac{r}{a_0}\right)_{max} = \frac{a}{a_0} = \frac{1\times10^{-15}\,m}{0.5\times10^{-10}\,m}$$

$$= 2\times10^{-5} << 1$$

~~Therefore~~

Therefore we can ~~safely~~ set $e^{-2r/a_0} \approx 1$. The first order correction to the energy is then

$$\Delta E = \frac{4e^2}{(4\pi\epsilon_0)a_0^3}\int_0^a \left(\frac{1}{r} - \frac{1}{a}\right) r^2\,dr$$

$$= \frac{4e^2}{(4\pi\epsilon_0)a_0^3}\left(\frac{1}{2}a^2 - \frac{1}{3}a^2\right)$$

$$= \frac{4e^2a^2}{(4\pi\epsilon_0)a_0^3}\cdot\frac{1}{6}$$

$$= \frac{4}{3}\cdot\left(\frac{e^2}{(4\pi\epsilon_0)2a_0}\right)\frac{a^2}{a_0^2}$$

$$\boxed{\Delta E = \frac{4}{3}E_H\frac{a^2}{a_0^2}}, \qquad E_H \equiv \frac{e^2}{(4\pi\epsilon_0)2a} = 13.6\,eV$$

Numerically

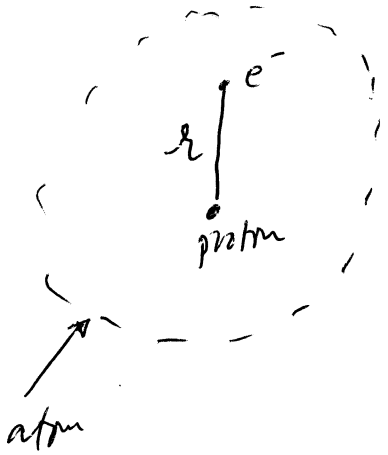
$$\Delta E = \frac{4}{3} \cdot (13.6\,eV) \left(\frac{1 \times 10^{-15}\,m}{0.5 \times 10^{-10}\,m} \right)^2$$

$$\approx 7 \times 10^{-9}\,eV.$$

The ground state has increased in energy, but the increase is very small.

Ex Calculate the shift in the ground state energy of the hydrogen atom if the proton is considered a uniform sphere of radius R instead of a point charge.

Ans

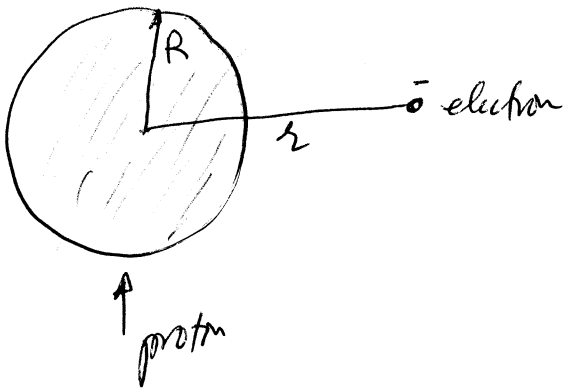


$$E_{1s}^{(0)} = \frac{-e^2}{4\pi\epsilon_0 2a_0} = -E_H = -13.6\,eV$$

$$\psi_{1s}^{(0)} = \frac{2}{\sqrt{4\pi}\, a_0^{3/2}} e^{-r/a_0}$$

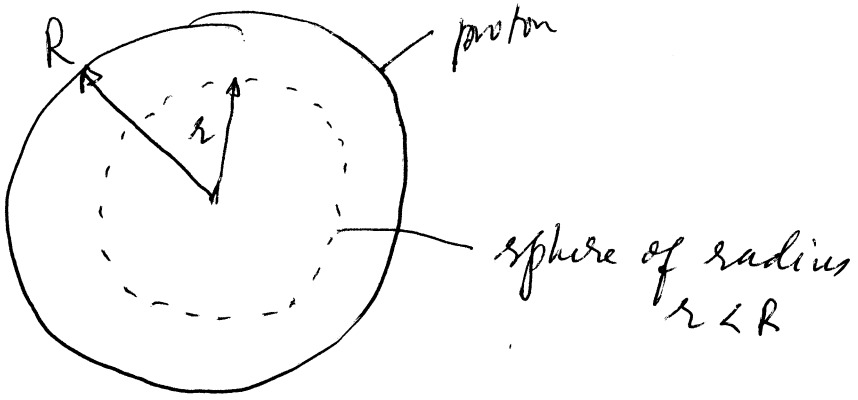
$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2}$$

Perturbed system.



$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \quad \text{for } r \geq R$$

Let us calculate the potential (not potential energy) of the electric field of the proton charge distribution for $r < R$.



Using Gauss's law for the sphere of radius $r < R$

$$E\,4\pi r^2 = \frac{q_{enclosed}}{\epsilon_0} = \frac{1}{\epsilon_0}\cdot\frac{4}{3}\pi r^3 \rho$$

$$= \frac{1}{\epsilon_0}\cdot\frac{4}{3}\pi r^3 \cdot \frac{e}{\frac{4}{3}\pi R^3}$$

$$= \frac{e r^3}{\epsilon_0 R^3}$$

$$\therefore \quad E = \frac{e r}{4\pi\epsilon_0 R^3}.$$

Let $v(r)$ be the potential. Therefore

$$\vec{E} = -\vec{\nabla} v$$

$$\text{or} \quad \frac{dv}{dr} = -\frac{e r}{4\pi\epsilon_0 R^3}$$

$$\therefore \quad v = \frac{-e r^2}{2(4\pi\epsilon_0) R^3} + C$$

Since $v(R) = \frac{e}{4\pi\epsilon_0 R}$,

$$\frac{e}{4\pi\epsilon_0 R} = -\frac{e}{2(4\pi\epsilon_0) R} + C$$

$$\therefore C = \frac{3e}{2(4\pi\epsilon_0) R}.$$

$$\therefore \quad v(r) = \frac{-e r^2}{2(4\pi\epsilon_0)R^3} + \frac{3e}{2(4\pi\epsilon_0)R}$$

$$\text{or,} \quad v(r) = \frac{e}{2(4\pi\epsilon_0)R}\left(3 - \frac{r^2}{R^2}\right) \quad (r < R)$$

Therefore, potential energy of the electron for $r < R$ is

$$V(r) = -e\,v(r) = -\frac{e^2}{2(4\pi\epsilon_0)R}\left(3 - \frac{r^2}{R^2}\right), \quad r < R$$

Thus,

$$V(r) = \begin{cases} \dfrac{-e^2}{2(4\pi\epsilon_0)R}\left(3 - \dfrac{r^2}{R^2}\right) & \text{for } r < R \\ -\dfrac{e^2}{4\pi\epsilon_0 r} & \text{for } r > R. \end{cases}$$

The perturbation is then

$$H' = V - V_0 \qquad \Big| \; V_0 = -\frac{e^2}{4\pi\epsilon_0 r} \text{ for all } r$$

$$= \begin{cases} -\dfrac{e^2}{4\pi\epsilon_0 R}\left(\dfrac{3}{2} - \dfrac{r^2}{2R^2}\right) + \dfrac{e^2}{4\pi\epsilon_0 r} & \text{for } r < R \\ 0 \quad \text{for } r > R \end{cases}$$

$$= \begin{cases} \dfrac{e^2}{4\pi\epsilon_0 R}\left(-\dfrac{3}{2} + \dfrac{r^2}{2R^2} + \dfrac{R}{r}\right) & r \leq R \\ 0 & \text{for } r \geq R \end{cases}.$$

Using this perturbation we can calculate the first order correction to the ground state energy in the previous problem.

$$E^{(1)} = \delta E^{(1)} = \langle \psi_{1s}^{(0)} | H' | \psi_{1s}^{(0)} \rangle$$

The ground state unperturbed wave function is

$$\psi_{1s}^{(0)}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \qquad | a_0 = \text{Bohr radius},$$

(independent of θ, φ)

$$\therefore \delta E^{(1)} = \frac{4\pi}{\pi a_0^3}\left(\frac{e^2}{4\pi\epsilon_0 R}\right)\int_0^R \left(-\frac{3}{2} + \frac{r^2}{2R^2} + \frac{R}{r}\right) e^{-2r/a_0} r^2 dr$$

Now $r_{max} = R = 10^{-15}\ m$

$a_0 \approx 10^{-10}\ m$

$\therefore$ $2r/a_0$ is very small

So $e^{-2r/a_0} \approx 1$.

The first order correction is then

$$\delta E^{(1)} = \frac{4\pi}{\pi a_0^3} \cdot \left(\frac{e^2}{4\pi\epsilon_0 R}\right)\int_0^R \left(-\frac{3}{2} + \frac{r^2}{2R^2} + \frac{R}{r}\right) r^2 dr$$

Carrying out the integral and simplifying we get

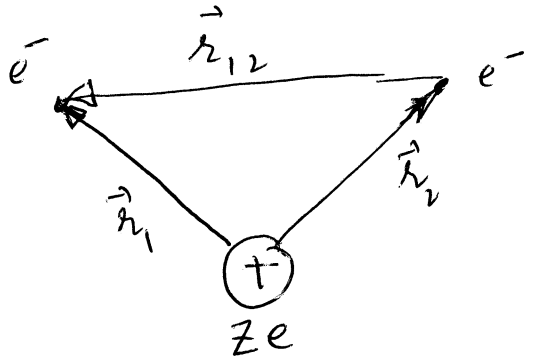
$$\delta E^{(1)} = \frac{4}{5}\left(\frac{e^2}{4\pi\epsilon_0 2a_0}\right)\frac{R^2}{a_0^2}$$

$$\propto \boxed{\delta E^{(1)} = \frac{4}{5} E_H \left(\frac{R^2}{a_0^2}\right)}$$

where

$$E_H = \frac{e^2}{(4\pi\epsilon_0) 2a_0} = 13.6\ eV$$

Ex Ground state of helium-type atoms.



$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$

The nucleus is taken to be a point charge with charge of Ze ($e = +ve = 1.6 \times 10^{-19} C$).

The Hamiltonian of the system is taken as

$$H = \underbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{H_0} + \underbrace{\frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}}_{V}$$

$$\therefore \quad H = H_0 + V$$

where the unperturbed Hamiltonian is

$$H_0 = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2}\right)$$

i.e.,

$$H_0 = H_0(1) + H_0(2).$$

The perturbing potential V is

$$V = \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} = \frac{e^2}{4\pi\epsilon_0 r_{12}}.$$

The unperturbed ground state energy is

$$E_0 = -\frac{Z^2 e^2}{(4\pi\epsilon_0) 2a_0} - \frac{Z^2 e^2}{(4\pi\epsilon_0) 2a_0}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} \quad \text{(Bohr radius)}$$

i.e., $$\boxed{E_0 = -2 Z^2 E_H}$$

where $$E_H = \frac{e^2}{(4\pi\epsilon_0) 2a_0} = 13.6 \text{ eV},$$

The corresponding unperturbed eigenfunction is the product of the eigenfunctions of each electron (neglect antisymmetry):

$$|E_0^{(0)}\rangle \doteq \psi_0 = \psi_{1s}(1)\,\psi_{1s}(2)$$

$$= \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Z r_1/a_0} \cdot \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Z r_2/a_0}$$

i.e., $\psi_0 = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-Z(r_1+r_2)/a_0}$

The first-order correction to energy is

$$E^{(1)} = \langle E_0^{(0)} | V | E_0^{(0)} \rangle$$

$$= \int \psi_0^*(r_1 r_2)\, V\, \psi_0(r_1 r_2)\, d^3r_1\, d^3r_2$$

$$= \frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^6 \int e^{-Z(r_1+r_2)/a_0} \cdot \frac{e^2}{4\pi\epsilon_0 r_{12}} \cdot e^{-Z(r_1+r_2)/a_0}\, d^3r_1\, d^3r_2$$

$$\propto E^{(1)} = \frac{e^2}{(4\pi\epsilon_0)\pi^2}\left(\frac{Z}{a_0}\right)^6 \int e^{-2Zr_1/a_0} \frac{1}{r_{12}} e^{-2Zr_2/a_0}\, d^3r_1\, d^3r_2$$

Let us now make changes in the variables of integration in the following manner:

$$\vec{\rho}_1 = \frac{2Z}{a_0}\vec{r}_1$$

$$\vec{\rho}_2 = \frac{2Z}{a_0}\vec{r}_2$$

Therefore

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = \frac{a_0}{2Z}|\vec{\rho}_1 - \vec{\rho}_2| = \frac{a_0}{2Z}\rho_{12}$$

$$d^3r_1 = \left(\frac{a_0}{2Z}\right)^3 d^3\rho_1$$

$$d^3r_2 = \left(\frac{a_0}{2Z}\right)^3 d^3\rho_2 .$$

With these change of variables $E^{(1)}$ can be written as

$$E^{(1)} = \frac{e^2}{(4\pi\epsilon_0)\pi^2}\cdot\left(\frac{Z}{a_0}\right)^6\cdot\frac{2Z}{a_0}\cdot\left(\frac{a_0}{2Z}\right)^6\int e^{-\rho_1}\frac{1}{\rho_{12}}e^{-\rho_2}d^3\rho_1 d^3\rho_2$$

Simplifying

$$E^{(1)} = \frac{e^2}{(4\pi\epsilon_0)\pi^2}\cdot\frac{2Z}{a_0}\cdot\frac{1}{2^6}\underbrace{\int e^{-(\rho_1+\rho_2)}\frac{1}{\rho_{12}}d^3\rho_1 d^3\rho_2}_{20\pi^2}$$

Now, we can show

$$\int \frac{e^{-(\rho_1+\rho_2)}}{\rho_{12}} d^3\rho_1 d^3\rho_2 = 20\pi^2.$$

Therefore, $E^{(1)}$ becomes

$$E^{(1)} = \frac{e^2}{(4\pi\epsilon_0)\pi^2} \frac{2Z}{a_0} \cdot \frac{1}{64} \cdot 20\pi^2$$

or $$E^{(1)} = \frac{5}{4} \cdot \frac{Ze^2}{(4\pi\epsilon_0) 2a_0}$$

i.e., $$\boxed{E^{(1)} = \frac{5}{4} \cdot Z E_H}$$

Hence, up to first order in perturbation theory,

$$E = E_0 + E^{(1)} = -2Z^2 E_H + \frac{5}{4} Z E_H$$

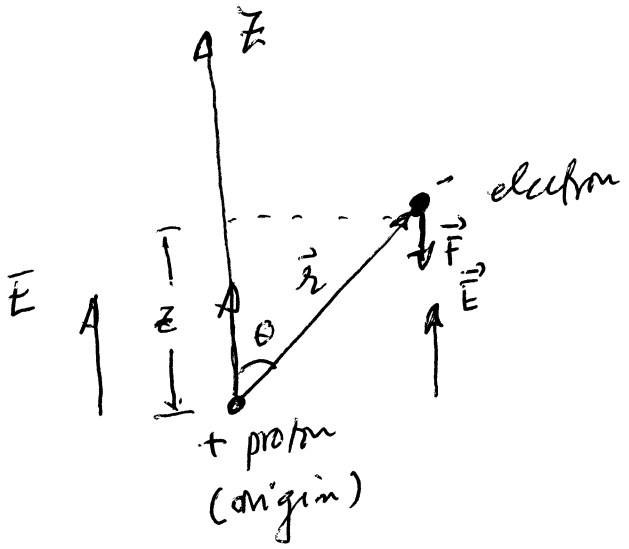
or $$\boxed{E = -\left(Z - \frac{5}{8}\right) 2Z E_H}$$

Example of degenerate perturbation theory

Stark effect in Hydrogen atom.

Stark effect is the splitting of atomic energy levels due to an applied electric field.

Let the electric field be uniform and along the z-axis.



The perturbation is

$$H' = |\vec{F}|z = |q_e|\bar{E}z = e\bar{E}z$$

$q_e = -e$
$e = 1.6\times10^{-19}\,C$
e is a +ve number

The unperturbed Hamiltonian is

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

The eigenvalues and eigenfunctions of H_0 are known.

$$H_0 \psi^{(0)}_{n\ell m}(\vec{r}) = E^{(0)}_n \psi^{(0)}_{n\ell m}(\vec{r})$$

with

$$E^{(0)}_n = -\frac{e^2}{(4\pi\epsilon_0)\, 2a_0}\,\frac{1}{n^2}\,; \quad n = 1, 2, 3, \ldots$$

$$a_0 = \frac{(4\pi\epsilon_0)\hbar^2}{m e^2} \quad (m = \text{mass of electron})$$

All levels (except the ground level) are degenerate.†

This is because for a given n

$$\ell = 0, 1, 2, \ldots (n-1)$$

and

$$m = -\ell, -\ell+1, \ldots \ell-1, \ell\,.$$

The ground state wave function is

$$\psi^{(0)}_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}}\, e^{-r/a_0}$$

which is independent of θ and φ.

---

† We neglect the spin degrees of freedom.

The first-order correction to the ground state energy is

$$E_{100}^{(1)} = \langle \psi_{100} | H' | \psi_{100} \rangle = 0$$

Level $n = 2$

The first excited state of the unperturbed hydrogen atom is four-fold degenerate, For $n = 2$, l can have values

$$l = 0, 1$$

For $l = 0$, $m = 0$, while for $l = 1$, $m = 1, 0, -1$.

The degenerate unperturbed eigenfunctions are

$$\psi_{200}^{(0)}, \psi_{210}^{(0)}, \psi_{211}^{(0)}, \psi_{21-1}^{(0)}.$$

A general unperturbed wave function is of the form

$$\psi_{nlm}^{(0)} = R_{nl}(r)\, Y_{lm}(\theta, \varphi).$$

We now have to diagonalize H' in the four-dimensional eigen subspace of $E_2^{(0)}$. The eigenvalues of H' are the first order correction to the energy and the eigenvectors of H' are the correct zero-order ~~correction to the wavefunction~~ approximation of the perturbed wave function.

Matrix representation of H'

Using the degenerate ~~eigen~~ zeroth-order wave functions $\psi_{200}^{(0)}$, $\psi_{210}^{(0)}$, $\psi_{211}^{(0)}$ and $\psi_{21-1}^{(0)}$ as basis we can work out the matrix for H'. We use the four wave functions in the following order

$$|1\rangle = |200\rangle \doteq \psi_{200}^{(0)}$$
$$|2\rangle = |210\rangle \doteq \psi_{210}^{(0)}$$
$$|3\rangle = |211\rangle \doteq \psi_{211}^{(0)}$$
$$|4\rangle = |21-1\rangle \doteq \psi_{21-1}^{(0)} . \quad \ldots (1)$$

A general matrix element of H' is of the form

$$\langle n l m | H' | n' l' m' \rangle \quad \text{with } n = 2.$$

Before working out the matrix elements, consider the following:

1. Suppose $l = l'$. This case includes all the diagonal elements ($m = m'$) and some non-diagonal elements ($m \neq m'$). In this case, the parity of the integrand of the matrix element is

$$(-1)^{2l+1} = -1 \text{ (odd)},$$

since $H' = eEz = eEr\cos\theta \sim Y_{21}$ has parity (-1). Therefore, the integral, i.e., the matrix element is zero.

2. Next, note that $H' = eEr\cos\theta$ is invariant under a rotation about the z-axis which only changes the azimuthal angle φ keeping

r and θ unchanged. Therefore

$$[H', L_z] = 0 .$$

Now, consider the matrix element of the commutator above:

$$\langle n l m | [H', L_z] | n l' m' \rangle = 0$$

or $$\langle n l m | H' L_z - L_z H' | n l' m' \rangle = 0$$

or $$(m' - m) \langle n l m | H' | n l' m' \rangle = 0$$

i.e., if $m' \neq m$, then

$$\langle n l m | H' | n l' m' \rangle = 0$$

The upshot of the arguments above is that $\langle n l m | H' | n l' m' \rangle = 0$ if $l = l'$ and if $m' \neq m$.

Thus all the matrix elements of H' except two are non-zero. These are

$$\langle 200|H'|210\rangle \quad \text{and} \quad \langle 210|H'|200\rangle$$

and these elements are complex conjugates of each other since H' is hermitian

Using the order of the unperturbed wave functions indicated above (Eq. (1)), the matrix representation of H' in the eigensubspace of $E_2^{(0)}$ is

$$H' \doteq \begin{array}{c} \\ \langle 1| \\ \langle 2| \\ \langle 3| \\ \langle 4| \end{array} \begin{array}{c} \begin{array}{cccc} |1\rangle & |2\rangle & |3\rangle & |4\rangle \end{array} \\ \begin{bmatrix} 0 & \langle 200|H'|210\rangle & 0 & 0 \\ \langle 210|H'|200\rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \end{array}$$

Calculation of $\langle 200|H'|210\rangle$

We have to calculate

$$\langle 200|H'|210\rangle$$

$$= \int \psi_{200}^{(0)*}(\vec{r})\, eEz\, \psi_{210}^{(0)}(\vec{r})\, d^3r$$

$$= eE\int \psi_{200}^{(0)*}(\vec{r})\, r\cos\theta\, \psi_{210}^{(0)}(\vec{r})\, d^3r$$

Now

$$\psi_{200}^{(0)} = R_{20}(r)\, Y_{00}(\theta\phi)$$

$$= \frac{1}{\sqrt{4\pi}} R_{20}(r)$$

$$= \frac{1}{\sqrt{4\pi}} \left(\frac{1}{2a_0}\right)^{3/2} (2 - r/a_0)\, e^{-r/2a_0}$$

$$\psi_{210}^{(0)} = R_{21}(r)\, Y_{10}(\theta\phi)$$

$$= \underbrace{\frac{1}{\sqrt{3}} \left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0}}_{R_{21}} \cdot \underbrace{\sqrt{\frac{3}{4\pi}}\cos\theta}_{Y_{10}}$$

i.e.,

$$\psi_{210}^{(0)} = \frac{1}{\sqrt{4\pi}} \left(\frac{1}{2a_0}\right)^{3/2} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos\theta .$$

$$\therefore \quad \langle 200 | H' | 210 \rangle$$

$$= eE \cdot \frac{1}{4\pi} \cdot \frac{1}{(2a_0)^3 a_0} \int_0^\infty r^4 (2 - r/a_0) e^{-r/a_0} dr \int_\Omega \cos^2\theta \sin\theta \, d\theta \, d\varphi$$

Now $$\int_0^{2\pi} d\varphi = 2\pi$$

$$\int_0^{\pi} \cos^2\theta \sin\theta \, d\theta = \int_{-1}^{+1} \mu^2 d\mu = \frac{2}{3} \qquad (\text{Substituting } \mu = \cos\theta)$$

Therefore

$$\langle 200 | H' | 210 \rangle$$

$$= \frac{eE}{4\pi (8a_0^3) a_0} \cdot (2\pi) \frac{2}{3} \int_0^\infty r^4 (2 - r/a_0) e^{-r/a_0} dr$$

$$= \frac{eE}{24 a_0^4} \int_0^\infty r^4 (2 - r/a_0) e^{-r/a_0} dr$$

Let

$$\frac{r}{a_0} = x$$

$$\therefore \quad \langle 200 | H' | 210 \rangle$$

$$= \frac{eE}{24 a_0^4} \int_0^\infty a_0^4 x^4 (2-x) e^{-x} a_0 dx$$

$$= \frac{eEa_0}{24} \int_0^\infty x^4 (2-x) e^{-x} dx$$

$$= \frac{eEa_0}{24} \left[2 \int_0^\infty x^4 e^{-x} dx - \int_0^\infty x^5 e^{-x} dx \right]$$

$$= \frac{eEa_0}{24} \left[2 \times 4! - 5! \right]$$

$$= \frac{eEa_0}{24} (48 - 120)$$

$$= \frac{eEa_0}{24} (-72)$$

$$= -3eEa_0$$

$$\int_0^\infty x^n e^{-x} dx = n!$$

n = integer

Hence

$$H' \doteq \begin{bmatrix} 0 & -3eEa_0 & 0 & 0 \\ -3eEa_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

The eigenvalues of H' are the first-order corrections to energy of the unperturbed $n=2$ levels of the hydrogen atom.

Eigenvalues of H'

The secular equation is

$$\det\left[\underline{H}' - E\,\underline{I}\right] = 0$$

or

$$\begin{vmatrix} -E & -3eEa_0 & 0 & 0 \\ -3eEa_0 & -E & 0 & 0 \\ 0 & 0 & -E & 0 \\ 0 & 0 & 0 & -E \end{vmatrix} = 0$$

$$\alpha \qquad E^2\left(E^2 - 9e^2E^2a_0^2\right) = 0$$

There are four roots of E. They are

$$E = -3eEa_0,\ 3eEa_0,\ 0,\ 0$$

Thus, the first-order corrections to the energy-level are

$$E_{21}^{(1)} = -3eEa_0,\quad E_{22}^{(1)} = 3eEa_0,\quad E_{23}^{(1)} = 0,\quad E_{24}^{(1)} = 0.$$

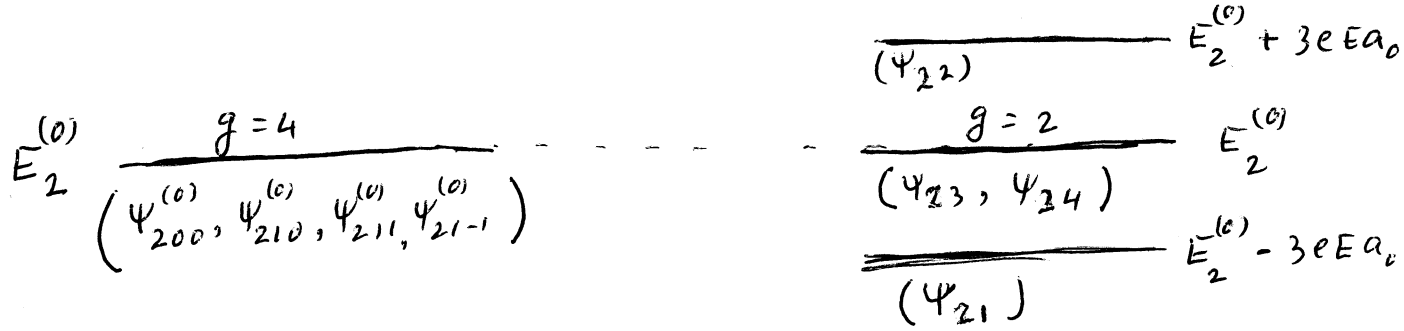


Fig: Splitting of the energy levels.

Eigenvectors of H in the zeroth order

The zeroth order eigenfunctions of H are the eigenvectors of H'. ~~Excluded block of H~~ There are four eigenvalues of H' (two of them are equal, namely zero). We have to find each eigenvector.

Eigenvalue $E_{n1}^{(1)} = -3eEa_0$ $(n=2)$

Let the eigenvector be (a_1, a_2, a_3, a_4). These components satisfy the equation

$$\begin{pmatrix} 3eEa_0 & -3eEa_0 & 0 & 0 \\ -3eEa_0 & 3eEa_0 & 0 & 0 \\ 0 & 0 & 3eEa_0 & 0 \\ 0 & 0 & 0 & 3eEa_0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = 0$$

Therefore we have

$$a_1 = a_2$$

$$a_3 = a_4 = 0.$$

the normalization condition we have $a_1 = a_2 = \frac{1}{\sqrt{2}}$.

The components $(a_1\ a_2\ a_3\ a_4)$ form the matrix representation of $\chi^{(0)}_{n1}$ in the basis $\{|1\rangle, |2\rangle, |3\rangle, |4\rangle\}$ where

$$|1\rangle = |200\rangle = \psi^{(0)}_{200}$$

$$|2\rangle = |210\rangle = \psi^{(0)}_{210}$$

$$|3\rangle = |211\rangle = \psi^{(0)}_{211}$$

$$|4\rangle = |21{-1}\rangle = \psi^{(0)}_{21-1}.$$

$$\therefore \quad \chi^{(0)}_{n1} = a_1 \psi^{(0)}_{200} + a_2 \psi^{(0)}_{210}$$

i.e $$\boxed{\chi^{(0)}_{n1} = \frac{1}{\sqrt{2}} \left(\psi^{(0)}_{200} + \psi^{(0)}_{210} \right)}$$

Eigenvalue $E_{n2}^{(1)} = +3eEa_0 \quad (n=2)$

The eigenvalue equation is

$$\begin{pmatrix} -3eEa_0 & -3eEa_0 & 0 & 0 \\ -3eEa_0 & -3eEa_0 & 0 & 0 \\ 0 & 0 & -3eEa_0 & 0 \\ 0 & 0 & 0 & -3eEa_0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = 0$$

We have $a_3 = a_4 = 0$

and $a_1 = -a_2 = \frac{1}{\sqrt{2}}$

$$\therefore \boxed{\chi_{n2}^{(0)} = \frac{1}{\sqrt{2}} \left(\psi_{200}^{(0)} - \psi_{210}^{(0)} \right)}$$

Eigenvalues $E_{n3}^{(1)} = E_{n4}^{(1)} = 0 \quad (n=2)$

The eigenvalue equation is

$$\begin{pmatrix} 0 & -3eEa_0 & 0 & 0 \\ -3eEa_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix} = 0$$

We have

$$a_1 = a_2 = 0$$

and a_3 and a_4 are arbitrary. Since we have two linearly independent eigenvectors, we can choose either

$$a_3 = 1 \text{ and } a_4 = 0$$

or

$$a_3 = 0 \text{ and } a_4 = 1.$$

Thus, the two linearly independent eigenvectors with degenerate eigenvalue 0 are:

$$\begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

These two linearly independent eigenvectors are normalized and orthogonal. In the Hilbert space the eigenvectors are

$$\chi^{(0)}_{23} = \psi^{(0)}_{211}$$

$$\chi^{(0)}_{24} = \psi^{(0)}_{21-1}$$

Thus finally