Degenerate Perturbation Theory

We learned that if

$$\hat{H} = \hat{H}_0 + \lambda \hat{V} \tag{1}$$

and the spectrum of $\hat{H}_0$ is non-degenerate then the perturbed eigenvalues and eigenvectors are

$$E_n \approx E_n^0 + \lambda \langle n_0 | \hat{V} | n_0 \rangle + \lambda^2 \sum_{m \neq n} \frac{|\langle m_0 | \hat{V} | n_0 \rangle|^2}{E_n^0 - E_m^0} \tag{2}$$

$$|n\rangle \approx |n_0\rangle + \lambda \sum_{m \neq n} \frac{|m_0\rangle \langle m_0 | \hat{V} | n_0 \rangle}{E_n^0 - E_m^0} \tag{3}$$

the eigenvalues are always one order ahead of the eigenvectors. Thus, the corrections up to first order would be

$$\begin{aligned} E_n &\approx E_n^0 + \lambda \langle n_0 | \hat{V} | n_0 \rangle \\ |n\rangle &\approx |n_0\rangle \end{aligned} \tag{4}$$

To lowest order, the eigenvectors do not change. This first order correction is very convenient because it is <u>local</u>: the change from E_n^0 to E_n involves simply computing the expectation value of the perturbation in the state unperturbed state. Since $|n_0\rangle$ and $|n\rangle$ must be normalized, there can be no change in the eigenvector.

Now we consider the case when $\hat{H}_0$ may contain degeneracies. A good example is the Hydrogen atom. The 1s state is not degenerate, but the 2s and 2p states are (the degeneracy is 4-fold).

When there is degeneracy we clearly see that we may run in trouble with the second order correction because of $1/(E_n^0 - E_m^0)$ which may explode.

However, the problem is even worse, because we also run into trouble with the first order correction in (4). The reason is that, if E_n^0 is degenerate, there will be more than one possible $|n_0\rangle$ to use in computing $\langle n_0|\hat{V}|n_0\rangle$. In fact, there are an infinite number of possibilities because any linear combination of the degenerate eigenvectors will also be an eigenvectors.

We will therefore take a step back and focus on fixing

Eq. (4)

2-fold degeneracy

Let us illustrate the problem supposing that a certain level has a two-fold degeneracy. Thus

$$\hat{H}_0 |a\rangle = E^\circ |a\rangle$$
$$\hat{H}_0 |b\rangle = E^\circ |b\rangle \qquad (5)$$

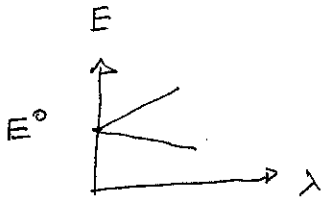
$|a\rangle$ and $|b\rangle$ are two eigenvectors of $\hat{H}_0$, both with energy E°. But they are not unique. In fact, any linear combination of $|a\rangle$ and $|b\rangle$ is also an eigenvector

$$|\phi_0\rangle = \alpha |a\rangle + \beta |b\rangle. \qquad (6)$$

what we want is to find the eigenvalues and eigenvectors of $\hat{H}$:

$$\hat{H} |\phi\rangle = E |\phi\rangle \qquad (7)$$

what we expect is that the perturbation will lift the degeneracy of E°



So we expect to find from Eq (7) two eigenvalues E_+ and E_-, and two eigenvectors, $|\phi_+\rangle$ and $|\phi_-\rangle$. When $\lambda \to 0$, E_+ and E_- will both tend to E°. But for which combination $\alpha|a\rangle + \beta|b\rangle$ will $|\phi_+\rangle$ and $|\phi_-\rangle$ tend to?

For example, if $\hat{H}_0 = \Delta \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ and $\hat{V} = \begin{bmatrix} 0 & \delta \\ \delta & 0 \end{bmatrix}$ then

$$\hat{H} = \begin{bmatrix} \Delta & \lambda\delta \\ \lambda\delta & \Delta \end{bmatrix}$$

so the eigenvalues and eigenvectors of $\hat{H}$ are

$$E_+ = \Delta + \lambda\delta \qquad |\phi_+\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$E_- = \Delta - \lambda\delta \qquad |\phi_-\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

Note how the eigenvectors don't even depend on λ, so if we make $\lambda \to 0$, $|\phi_+\rangle$ and $|\phi_-\rangle$ will each tend to specific linear combinations of $|a\rangle$ and $|b\rangle$.

The idea is the same as before: we expand both E and $|\phi\rangle$ in a power series in λ:

$$E = E^0 + \lambda E^1 + \lambda^2 E^2 + \dots$$
$$|\phi\rangle = |\phi_0\rangle + \lambda|\phi_1\rangle + \lambda^2|\phi_2\rangle + \dots \quad (8)$$

But now we don't even know what $|\phi_0\rangle$ should be. Thus, we will stick only to first order terms. Inserting (8) in (7) we get

$$(\hat{H}_0 + \lambda\hat{V})(|\phi_0\rangle + \lambda|\phi_1\rangle) = (E_0 + \lambda E_1)(|\phi_0\rangle + \lambda|\phi_1\rangle)$$

The term of order λ^0 is

$$H_0|\phi_0\rangle = E^0|\phi_0\rangle$$

which is trivially satisfied. The term of order λ^1 is

$$\hat{H}_0|\phi_1\rangle + \hat{V}|\phi_0\rangle = E^0|\phi_1\rangle + E^1|\phi_0\rangle \quad (9)$$

Now we take the inner product with $\langle a|$:

$$\langle a|\hat{H}_0|\phi_1\rangle + \langle a|\hat{V}|\phi_0\rangle = E^0\langle a|\phi_1\rangle + E^1\langle a|\phi_0\rangle$$

$\langle a|\hat{H}_0|\phi_1\rangle = E_0\langle a|\phi_1\rangle$

Thus

$$\langle a|\hat{V}|\phi_0\rangle = E^1\langle a|\phi_0\rangle \quad (10a)$$

If, instead, we take the inner product with $\langle b|$, we get

$$\langle b|\hat{H}_0|\phi_1\rangle + \langle b|\hat{V}|\phi_0\rangle = E^0\langle b|\phi_1\rangle + E^1\langle b|\phi_0\rangle$$

$\langle b|\hat{H}_0|\phi_1\rangle = E_0\langle b|\phi_1\rangle$

so

$$\langle b|\hat{V}|\phi_0\rangle = E^1\langle b|\phi^0\rangle \tag{10b}$$

Finally we substitute $|\phi_0\rangle = \alpha|a\rangle + \beta|b\rangle$, and also recall that $\alpha = \langle a|\phi_0\rangle$ and $\beta = \langle b|\phi_0\rangle$. Then

$$\begin{aligned}\alpha\langle a|\hat{V}|a\rangle + \beta\langle a|\hat{V}|b\rangle &= \alpha E^1 \\ \alpha\langle b|\hat{V}|a\rangle + \beta\langle b|\hat{V}|b\rangle &= \beta E^2\end{aligned} \tag{11}$$

Note how the whole thing depends on the matrix elements of $\hat{V}$ in the basis of eigenvectors whose eigenvalue is E^0;

$$\begin{aligned}V_{aa} &= \langle a|\hat{V}|a\rangle \\ V_{ab} &= \langle a|\hat{V}|b\rangle\end{aligned} \tag{12}$$

etc.

We can also write (11) as an eigenvalue/eigenvector equation

$$\begin{bmatrix} V_{aa} & V_{ab} \\ V_{ba} & V_{bb} \end{bmatrix}\begin{bmatrix}\alpha \\ \beta\end{bmatrix} = E^1\begin{bmatrix}\alpha \\ \beta\end{bmatrix} \tag{13}$$

where, note, $V_{ba} = V_{ab}^*$.

Thus, we see that if we start with a 2-fold degeneracy, we expect after the perturbation to obtain two distinct eigenvalues. These eigenvalues will then be

$$\begin{aligned}E_+ &= E^0 + \lambda E_+^1 \\ E_- &= E^0 + \lambda E_-^1\end{aligned} \tag{14}$$

where $E_\pm^1$ are the eigenvalues of Eq (13)

Moreover, the eigenvectors obtained from Eq (13) will be the correct combinations $\alpha|a\rangle + \beta|b\rangle$ that $|\phi_+\rangle$ and $|\phi_-\rangle$ will tend to when $\lambda \to 0$.

Hence, we fixed Eq (4) so that it also works with for degenerate levels.

The whole thing rests in finding the eigenvalues of the matrix

$$\hat{W} = \begin{bmatrix} V_{aa} & V_{ab} \\ V_{ba} & V_{bb} \end{bmatrix} \tag{15}$$

whose entries are

$$W_{ij} = \langle i | \hat{V} | j \rangle \tag{16}$$

where $|i\rangle$ are a set of eigenvectors of $\hat{H}_0$ with the same eigenvalue.

Generalization to g-fold degeneracy

It is very straightforward to generalize everything for the case where the degeneracy is not 2-fold, but g-fold. For, everything we did would also hold if $|\phi_0\rangle$ were a linear combination of more than 2 vectors.

Now we assume a certain level E^0 of $\hat{H}_0$ is g-fold degenerate, so that there exists g linearly independent vectors $|i\rangle$ such that

$$\hat{H}_0 |i\rangle = E^0 |i\rangle \tag{17}$$

We also choose the $|i\rangle$ to form an orthonormal basis. Then, to find the perturbed eigenvalues and eigenvectors we must construct the matrix $\hat{W}$ with entries

$$W_{ij} = \langle i | \hat{V} | j \rangle \tag{18}$$

This matrix will be $g \times g$. Define

$$\hat{W} |\phi_k\rangle = w_k |\phi_k\rangle , \quad k = 1, \ldots, g \tag{19}$$

Then the perturbed eigenvalues of $\hat{H}$ will be

$$E_k \approx E^0 + \lambda w_k \tag{20}$$

and the perturbed eigenvectors will be

$$|\phi_k\rangle = \sum_i |i\rangle \langle i | \phi_k \rangle \tag{21}$$

which means that $|\phi_k\rangle$ will only have, at most, g entries.

Example

A few months ago I ran into the following problem in my research. I had a $2N$-dimensional Hilbert space with a basis that I chose to label as

$$|k,0\rangle \text{ and } |0,k\rangle \tag{22}$$

where $k = 1, \ldots, N$. In this basis I had a Hamiltonian which was diagonal

$$\hat{H}_0 |k,0\rangle = E_k^0 |k,0\rangle$$
$$\hat{H}_0 |0,k\rangle = E_k^0 |0,k\rangle \tag{23}$$

the energies E_k^0 were some functions which I knew, and they were all distinct. Hence, each level E_k^0 was 2-fold degenerate because both $|k,0\rangle$ and $|0,k\rangle$ had the same energy.

For this reason, the $2N \times 2N$ matrix $\hat{H}_0$ was separated into N blocks of size 2×2, each with energy E^0.

I then applied a perturbation so I wanted the eigenvalues and eigenvectors of

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}$$

Since each subspace is 2×2, to solve this problem we need to diagonalize N matrices $\hat{W}$, one for each 2×2 subspace.

Hence, define

$$\hat{W}_k = \begin{bmatrix} \langle k,0|\hat{V}|k,0\rangle & \langle k,0|\hat{V}|0,k\rangle \\ \langle 0,k|\hat{V}|k,0\rangle & \langle 0,k|\hat{V}|0,k\rangle \end{bmatrix}$$

For my particular problem it turned out that the diagonal entries were zero and the off-diagonal entries were real (this is actually very common). Thus I had

$$\hat{W}_k = \begin{bmatrix} 0 & G_k \\ G_k & 0 \end{bmatrix} \tag{24}$$

where G_k were certain functions that I knew. The eigenvalues and eigenvectors of this matrix are

$$w_k^+ = G_k \qquad |\phi_k^+\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$w_k^- = -G_k \qquad |\phi_k^-\rangle = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix} \tag{25}$$

Hence, the perturbed eigenvalues and eigenvectors were

$$E_k^+ = E_k^0 + G_k \qquad |\phi_k^+\rangle = \frac{|k,0\rangle + |0,k\rangle}{\sqrt{2}}$$

$$E_k^- = E_k^0 - G_k \qquad |\phi_k^-\rangle = \frac{|k,0\rangle - |0,k\rangle}{\sqrt{2}} \tag{26}$$

Note that $k = 1, \ldots, N$ so that we still have $2N$ eigenvalues and eigenvectors. But for $\lambda = 0$, they were degenerate in pairs. When the interaction is turned on, it lifts the degeneracy of each pair.

A very useful theorem

Let us go back to the 2-fold case. Suppose we work out the matrix $\hat{V}$ in Eq (15) and surprisingly find that

$$V_{ab} = 0 \tag{27}$$

(which implies $V_{ba} = 0$). This means that

$$\hat{V} = \begin{bmatrix} V_{aa} & 0 \\ 0 & V_{bb} \end{bmatrix} \tag{28}$$

the perturbed eigenvalues are then very simple

$$E_+ = E^0 + \lambda V_{aa} = E^0 + \lambda \langle a|\hat{V}|a\rangle \qquad (2$$

$$E_- = E^0 + \lambda V_{bb} = E^0 + \lambda \langle b|\hat{V}|b\rangle$$

But if we look closely, this is again Eq (4), so we could have used non-degenerate perturbation theory (which is easier).

Thus, if it were possible to know in advance that $V_{ab} = 0$, we can skip alot of work and go straight to Eq. (4). But this requires making a good initial choice for $|a\rangle$ and $|b\rangle$, because there are infinitely many choices and only one will lead to Eq (28).

Of course, this "good choice" is nothing but the perturbed eigenvectors $|\phi_+\rangle$ and $|\phi_-\rangle$, since if we use them as basis, $\hat{V}$ will be diagonal.

Now here is a very useful theorem. Suppose there is some operator $\hat{A}$ such that

$$[\hat{A}, \hat{H}_0] = [\hat{A}, \hat{V}] = 0 \tag{30}$$

(consequently $[\hat{A}, \hat{H}] = 0$). Then we may diagonalize $\hat{A}$ and $\hat{H}_0$ simultaneously. Regarding our choices of $|a\rangle$ and $|b\rangle$, we may now choose the ones that are also eigenvectors of $\hat{A}$:

$$\begin{aligned} \hat{A}|a\rangle &= \lambda_a |a\rangle \\ \hat{A}|b\rangle &= \lambda_b |b\rangle \end{aligned} \tag{31}$$

Suppose, in addition, that $\lambda_a \neq \lambda_b$. Then, since $[\hat{A}, \hat{V}] = 0$,

$$\begin{aligned} 0 = \langle a|[\hat{A}, \hat{V}]|b\rangle &= \langle a|\hat{A}\hat{V}|b\rangle - \langle a|\hat{V}\hat{A}|b\rangle \\ &= (\lambda_a - \lambda_b)\langle a|\hat{V}|b\rangle \end{aligned}$$

Since $\lambda_a \neq \lambda_b$ we then get

$$\langle a|\hat{V}|b\rangle = 0. \tag{32}$$

<u>Conclusion</u>: if E° is degenerate, but you can choose as eigenvectors those vectors which also diagonalize some observables $\hat{A}$, then you may go straight to non-degenerate perturbation theory. Your choice of eigenvectors will have been the <u>good ones</u>, in the sense that $\hat{V}$ will already be diagonal.

We proved this theorem for 2-fold degeneracy. But it also holds for the general case. The proof is very similar.

Example: perturbed 3D infinite well

The 3D infinite well with sides a has eigenfunctions

$$\psi_{n_x, n_y, n_z} = \psi_{n_x}(x)\,\psi_{n_y}(y)\,\psi_{n_z}(z) \tag{33}$$

where

$$\psi_n(x) = \sqrt{\frac{2}{a}}\,\sin\left(\frac{n\pi x}{a}\right) \tag{34}$$

The corresponding eigenenergies are

$$E^0_{n_x, n_y, n_z} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{35}$$

The ground state is

$$E^0_{111} = 3\,\frac{\pi^2\hbar^2}{2ma^2} \tag{36}$$

and it is not degenerate. The wavefunction is ψ_{111}.

But the first excited state is degenerate. The energy is

$$E^0_{112} = 6\,\frac{\pi^2\hbar^2}{2ma^2} \tag{37}$$

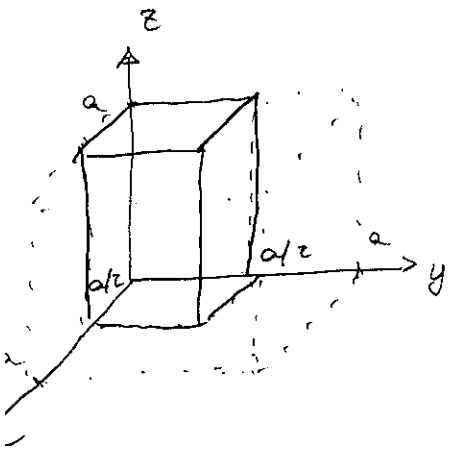
and the eigenfunctions are

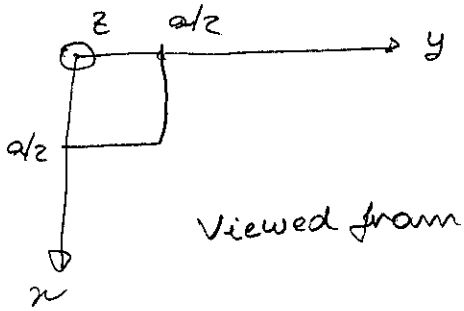
$$\psi_a = \psi_{112} \qquad \psi_b = \psi_{121} \qquad \psi_c = \psi_{211} \tag{38}$$

Suppose we now apply a perturbation

$$V = \begin{cases} V_0 & x \in [0, a/2] \text{ and } y \in [0, a/2] \\ 0 & \text{otherwise} \end{cases} \tag{39}$$

This means





Viewed from above.

Essentially, we are shifting the "floor" by an amount V_0 in a volume which is 1/4 of the total volume of the box. If we had shifted the entire box, the only difference would be to shift the energy by V_0.

If we treat V_0 as a perturbation, then for the ground state we may use non-degenerate perturbation theory

$$E^1_{111} = \langle 111 | V | 111 \rangle = \int_0^a dx \int_0^a dy \int_0^a dz \; V(x,y,z) \, |\psi_{111}|^2$$

$$= V_0 \int_0^{a/2} dx \, |\psi_1(x)|^2 \int_0^{a/2} dy \, |\psi_1(y)|^2 \int_0^a dz \, |\psi_1(z)|^2 \tag{40}$$

the functions $\psi_n(x)$ form an orthonormal basis in the sense that

$$\int_0^a \psi_m^*(x)\,\psi_m(x)\,dx = \delta_{mm} \tag{41}$$

Thus, the third term in (40) is 1. The other two terms must be computed by hand. I will leave as an exercise for you to show that

$$\int_0^{a/2} |\psi_n(x)|^2 dx = \frac{2}{a}\int_0^{a/2} \sin^2\left(\frac{n\pi x}{a}\right)dx = 1/2 \quad \text{for any } n \tag{42}$$

Thus Eq (40) becomes

$$E^1_{111} = \frac{V_0}{4} \tag{43}$$

which is sort of intuitive.

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Now let us look at the first excited state. We need to compute the matrix $\hat{W}$, which will be 3×3 since the degeneracy is 3-fold.

We start with the diagonal entries:

$$V_{aa} = \langle 112|V|112\rangle = V_0 \int_0^{a/2} dx\,|\psi_1(x)|^2 \int_0^{a/2} dy\,|\psi_1(y)|^2 \int_0^{a} dz\,|\psi_2(3)|^2$$

Because of (41) and (42), we will have $V_{aa} = V_0/4$.

In fact, the same will happen for the other diagonal elements

$$V_{aa} = V_{bb} = V_{cc} = \frac{V_0}{4} \tag{44a}$$

Now we look at the off-diagonal elements V_{ab}, V_{ac} and V_{bc}:

$$V_{ab} = \langle 11|\hat{V}|12\rangle = V_0 \int_0^{a/2} dx\, |\psi_1(x)|^2 \int_0^{a/2} dy\, \psi_1(y)\psi_2(y) \int_0^{a} dz\, \psi_2(z)\psi_1(z)$$

But in the z-integral we are integrating from 0 to a, so in this part the orthogonality relation in (41) holds. Whence

$$V_{ab} = 0 \tag{44b}$$

The same will be true for

$$V_{ac} = \langle 11|\hat{V}|21\rangle = 0 \tag{44c}$$

But not for

$$V_{bc} = \langle 12|\hat{V}|21\rangle = V_0 \int_0^{a/2} dx\, \psi_1(x)\psi_2(x) \int_0^{a/2} dy\, \psi_2(y)\psi_1(y) \underbrace{\int_0^{a} dz\, \psi_1^2(z)}_{1}$$

The two remaining integrals are identical and they must be computed by hand:

$$\int_0^{a/2} dx\, \psi_1(x)\psi_2(x) = \frac{4}{3\pi}$$

Hence

$$V_{bc} = \frac{16\, V_0}{9\pi^2} \tag{44d}$$

Combining everything we finally obtain the W matrix

$$W = \frac{V_0}{4}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \delta \\ 0 & \delta & 1 \end{bmatrix} \tag{45}$$

where

$$\delta = \frac{64}{9\pi^2} \approx 0.7205$$

The eigenvalues and eigenvectors of W are easy to compute because the lower part is $1 + \delta\sigma_x$. Thus

$$\begin{aligned} w_1 &= \frac{V_0}{4} & |\phi_1\rangle &= \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \\ w_2 &= \frac{V_0}{4}(1+\delta) & |\phi_2\rangle &= \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ 1 \\ 1 \end{bmatrix} \\ w_3 &= \frac{V_0}{4}(1-\delta) & |\phi_3\rangle &= \frac{1}{\sqrt{2}}\begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} \end{aligned} \tag{46}$$

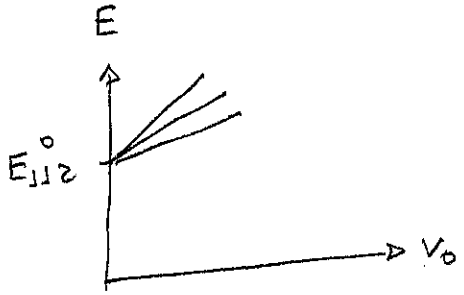
Hence, the perturbed energies are

$$E^0_{112} + \frac{V_0}{4}$$
$$E^0_{112} + \frac{V_0}{4}(1+\delta) \qquad (47)$$
$$E^0_{112} + \frac{V_0}{4}(1-\delta)$$

whereas the perturbed eigenvectors are

$$\psi_{112}$$
$$\frac{\psi_{121} + \psi_{211}}{\sqrt{2}} \qquad (48)$$
$$\frac{\psi_{121} - \psi_{211}}{\sqrt{2}}$$

Since $\delta < 1$, the 3 perturbed eigenvalues are larger than E^0_{112}. But only one is larger by an amount $\frac{V_0}{4}$, as observed in the non-degenerate case. The others contain a weird term $\delta = 64/9\pi^2$.



The Stark Effect

This section is a tribute to Ned Stark and Game of Thrones, which will premier in 5 days (from the moment I am writting these notes).

The Stark effect is the change in the energy levels of an atom or molecule due to the presence of an electric field. We will assume that this field points in the z direction, and we will consider (for obvious reasons) the case of hydrogen. Thus, the complete Hamiltonian is

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} - e\mathcal{E}z \tag{49}$$

we will assume that $\mathcal{E}$ is small so that we may treat it as a perturbation

$$V = -e\mathcal{E}z \tag{50}$$

The ground state 1s is not degenerate so we may compute the first order correction using non-degenerate theory. The ground-state eigenfunction is

$$\psi_{100} = \frac{1}{\sqrt{\pi}}e^{-r} \tag{51}$$

where I am setting $a_0 = 1$. We can put back a_0 in the final result. I will explain how.

We then have

$$E_1^1 = \langle 100|V|100\rangle = -e\mathcal{E}\int |\psi_{100}|^2 z\, dV$$

Set $z = r\cos\theta$ and $dV = r^2\sin\theta\, dr\, d\theta\, d\phi$ so the θ-integral will be

$$\int_0^\pi \sin\theta\cos\theta\, d\theta = \int_{-1}^{1} s\, ds = 0$$

$$s = \cos\theta$$

Hence, the first order correction to the energy of the ground state is zero

$$E_1^1 = 0 \tag{52}$$

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Next we look at the first excited state. It is 4-fold degenerate because 2s and the 3 2p levels all have energy E_2. Thus we need to use degenerate perturbation theory and find the matrix W in this 4×4 subspace with

$$\psi_a = \psi_{200} = \frac{(2-r)}{4\sqrt{2\pi}}\, e^{-r/2} \tag{53a}$$

$$\psi_b = \psi_{210} = \frac{r}{4\sqrt{2\pi}}\, e^{-r/2}\cos\theta \tag{53b}$$

$$\psi_c = \psi_{211} = -\frac{r}{8\sqrt{\pi}}\, e^{-r/2} e^{i\phi}\sin\theta \tag{53c}$$

$$\psi_d = \psi_{21,-1} = \frac{r}{8\sqrt{\pi}}\, e^{-r/2} e^{-i\phi}\sin\theta \tag{53d}$$

We start with the diagonal entries

$$V_{aa} = -e\mathcal{E}\int |\psi_{200}|^2 z\, dV$$

$$= -\frac{e\mathcal{E}}{32\pi}\int (2-r)^2 e^{-r}\,(r\cos\theta)\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

Note again the same integral in θ, which is again zero. Thus

$$V_{aa} = 0$$

Next

$$V_{bb} = -\frac{e\mathcal{E}}{32\pi}\int r^2 e^{-r}\cos^2\theta\,(r\cos\theta)\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

Again we have

$$\int_0^{\pi} \cos^3\theta\sin\theta\, d\theta = \int_{-1}^{1} s^3\, ds = 0$$

So $V_{bb} = 0$.

Next:

$$V_{cc} = -\frac{e\mathcal{E}}{64\pi}\int r^2 e^{-r}\sin^2\theta\,(r\cos\theta)\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$\int_0^{\pi} \sin^2\theta\cos\theta\sin\theta\, d\theta = \int_{-1}^{1}(1-s^2)\, s\, ds = 0$$

So $V_{cc} = 0$. Since ψ_d has the same dependence in θ, $V_{dd} = 0$. Thus, all diagonal elements are zero.

Next we look at the off-diagonal elements

$$V_{ab},\quad V_{ac},\quad V_{ad},\quad V_{bc},\quad V_{bd},\quad V_{cd}.$$

First:

$$V_{ab} = -e\mathcal{E}\int \psi_{200}^{*}\,\psi_{210}\; z\, dV$$

$$= -\frac{e\mathcal{E}}{32\pi}\int (2-r)\, r\, e^{-r}\cos\theta\,(r\cos\theta)\, r^{2}\sin\theta\, dr\, d\theta\, d\phi$$

$$= -\frac{e\mathcal{E}}{32\pi}\int_{0}^{\infty}(2-r)\, r^{4}\, e^{-r}\, dr \int_{0}^{\pi}\cos^{2}\theta\,\sin\theta\, d\theta \underbrace{\int_{0}^{2\pi} d\phi}_{2\pi}$$

We have $$\int_{0}^{\pi}\cos^{2}\theta\,\sin\theta\, d\theta = \int_{-1}^{1} s^{2}\, ds = \frac{s^{3}}{3}\Big|_{-1}^{1} = \frac{2}{3}$$

Also, recall that

$$\int_{0}^{\infty} r^{n}\, e^{-r}\, dr = n! \qquad (54)$$

Then $$\int_{0}^{\infty}(2-r)\, r^{4}\, e^{-r}\, dr = 2(4!) - 5! = -72$$

Thus $$V_{ab} = -\frac{e\mathcal{E}}{32\pi}(-72)\,\frac{2}{3}\,2\pi = 3\,e\,\mathcal{E}$$

Next

$$V_{ac} = -qE \int \psi_{200}^{*} \psi_{211} z \, dV$$

$$= -\frac{qE(-1)}{32\pi\sqrt{2}} \int (2-r) r e^{-r} e^{i\phi} \sin\theta (r\cos\theta) r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Now we have an integral in ϕ, for the first time:

$$\int_0^{2\pi} e^{i\phi} d\phi = 0$$

Thus $V_{ac} = 0$.

This integral will occur in V_{ad}, V_{bc}, V_{bd}. So these are <u>all</u> zero. The last one we need to look at

$$V_{cd} = -\frac{qE(-1)}{64\pi} \int r^2 e^{-r} \sin^2\theta (r\cos\theta) r^2 \sin\theta \, dr \, d\theta \, d\phi$$

But now we again obtain a zero from the θ integral.

Thus, the only non-zero entries of the entire W matrix are

$$W = 3eE \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \qquad (55)$$

We know how to diagonalize this matrix because the upper part is just σ_x. Thus

$$\omega_1 = 3 e \mathcal{E} \qquad |\phi_1\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \\ 0 \\ 0 \end{bmatrix}$$

$$\omega_2 = -3 e \mathcal{E} \qquad |\phi_2\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \\ 0 \\ 0 \end{bmatrix} \tag{56}$$

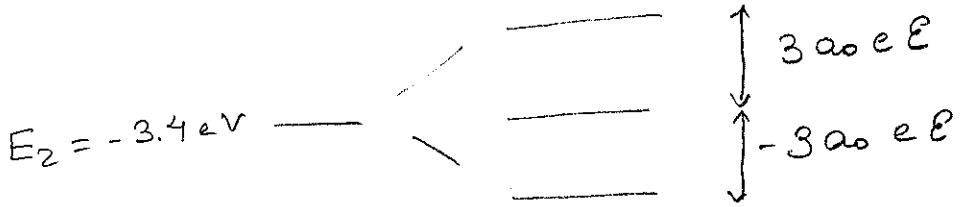
$$\omega_3 = \omega_4 = 0 \qquad |\phi_3\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} \quad |\phi_4\rangle = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

But these eigenvalues don't have units of energy because we set $a_0 = 1$. The product $e\mathcal{E}$ has units of force and energy is force times distance so the correct expressions are

$$\omega_1 = 3 a_0 e \mathcal{E} \tag{57}$$

$$\omega_2 = -3 a_0 e \mathcal{E}$$

Thus we conclude that the electric field splits the 4 degenerate levels into 3



This splitting will usually be very small. In electron-volts the energy difference is $3 a_0 \mathcal{E}$ and $a_0 = 5 \times 10^{-11}\,m$. So for moderate fields the splitting will be much smaller than 3.4 eV.