He atom

$1s^2$ can mix with $2s^2, 2p^2\ ({p_x}^2 + {p_y}^2 + {p_z}^2)$,

$3s^2, 2s3s, 2p3p, 3d^2,$ etc.

Mixing with 2s2p, 2s3d, 2p3d, etc. is forbidden by symmetry.

Variational treatment

Hylleras: $e^{-\xi r_1/a_0}\, e^{-\xi r_2/a_0}\, (1 + br_{12})$

$\rightarrow E = -78.7\text{eV},$ only 0.3eV in error

The best treatment is believed to give an energy connect to 50 significant figures (with relativistic and nuclear motion corrections)

We are not going to go through the equations for degenerate PT.

We can always treat such problems using a CI (matrix eigenvalue) approach

E.g. the mixing of the 2*s* and $2p_z$ orbitals of the H atoms due to the presence of a uniform electric field in the z direction

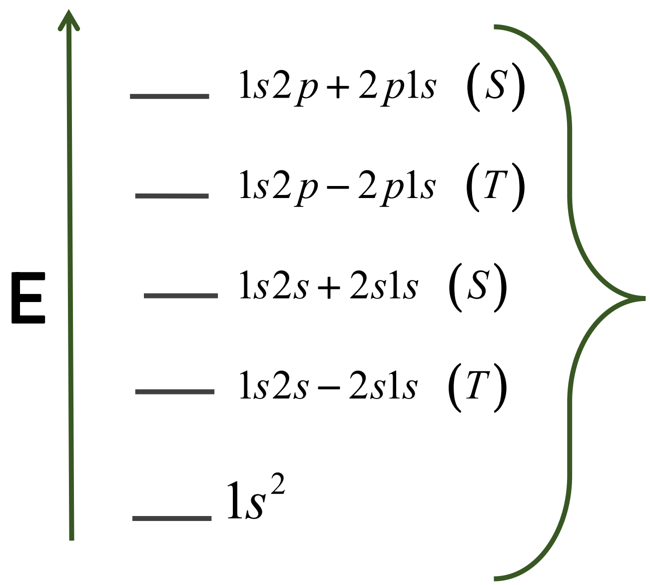
$H = H^0 + e\varepsilon z$, where H^0 is the H atom Hamiltonian.

$$\mathbf{H} = \begin{pmatrix} E_{2s} & H_{2s,2p_z} \\ H_{2s,2p_z} & E_{2p_z} \end{pmatrix} = \begin{pmatrix} E_{2s} & V \\ V & E_{2s} \end{pmatrix}$$

So $E = E_{2s} \pm V, \quad V = \langle 2s \,|\, e\varepsilon z \,|\, 2p_z \rangle$

The text treats the lowest energy excited states of Helium starting from an 8 fold degeneracy.

I believe it is more useful to first consider what the Pauli principle (electrons are fermions) tells us about acceptable forms of the wavefunctions.



Note the splitting of the $2s$, $2p$ degeneracy. The $2s$ electron is not as strongly shielded from the nucleus by the $1s$ electron as is the $2p$ electron.

Time-dependent PT

$$\hat{H} = \hat{H}^0 + \hat{H}'(t) \quad \text{where} \quad \hat{H}^0 \psi_k{}^0 = E_k{}^0 \psi_k{}^0$$

If we ignore $H'(t)$: $-\frac{\hbar}{i}\frac{\partial \Psi^0}{\partial t} = \hat{H}^0 \Psi^0$

Stationary state solutions

$$\Psi_k{}^0 = e^{-iE_k^0 t/\hbar} \psi_k{}^0$$

general solution

$$\Psi^0 = \sum_k c_k \Psi_k{}^0 = \sum c_k e^{-iE_k^0 t/\hbar} \psi_k^0$$

Now add $\hat{H}'(t)$

Ψ^0 no longer a solution

$$\Psi = \sum_k b_k \Psi_k^0$$

where the b_k can depend on t

$$\frac{db_m}{dt} = \frac{-i}{\hbar} \sum_k b_k e^{i\left(E_m{}^0 - E_k{}^0\right)t/\hbar} \left\langle \psi_m{}^0 \mid H' \mid \psi_k{}^0 \right\rangle$$

Suppose H'=0 for t < 0, and that at those times the system is stationary state with energy E_n^0

$$\text{I.e., for } t \le 0 : \Psi = e^{-iE_n{}^0 t/\hbar} \psi_n{}^0$$

$$b_n(0) = 1$$

$$b_k(0) = 0, k \ne n$$

Thus for short time

$$\frac{db_m}{dt} = \frac{-i}{\hbar} e^{i\left(E_m{}^0 - E_n{}^0\right)t/\hbar} \left\langle \psi_m{}^0 \mid \hat{H}' \mid \psi_n{}^0 \right\rangle$$

if H' acts until t'

$$b_m(t') = \delta_{mn} - \int_0^{t'} e^{i\left(E_m{}^0 - E_n{}^0\right)t/\hbar} \left\langle \psi_m{}^0 \mid H' \mid \psi_n{}^0 \right\rangle dt$$

$$t > t', \;\; b_m = b_m(t')$$

turning on the perturbation results in a super position of states.

$$\Psi = \sum_m b_m(t') e^{-iE_m{}^0 t/\hbar} \psi_m{}^0$$

If E field is in the x direction the force on charge Q_i is

$$Q_i \varepsilon_x = -\partial V / \partial x$$

$$V = -Q_i \varepsilon_x x$$

If there are several charges

$$V = -\sum_i Q_i x_i \varepsilon_x$$

If electromagnetic wave is traveling in the z direction

$$\varepsilon_x = \varepsilon_0 \sin\left(2\pi \nu t - 2\pi z / \lambda\right)$$

$$b_m(t') \approx \delta_{mn} + \frac{i\varepsilon_0}{\hbar}\int_0^{t'} e^{i\omega_{nm}t} \left\langle \psi_m{}^0 \,|\, \sum_i Q_i x_i \sin\left(\omega t - \frac{2\pi z_i}{\lambda}\right) |\, \psi_n{}^0 \right\rangle dt$$

In general, $\frac{2\pi z_i}{\lambda} << 1$

$$b_m\left(t'\right) \approx \delta_{mn} + \frac{\varepsilon_0}{2\hbar}\left\langle \psi_m{}^0 \,|\, \sum_i Q_i x_i \,|\, \psi_n{}^0 \right\rangle \int_0^{t'} e^{i\left(\omega_{nm}+\omega\right)t} - e^{i\left(\omega_{nm}-\omega\right)t} dt$$

$$b_m\left(t'\right) = \delta_{mn} + \frac{\varepsilon_0}{2\hbar i}\left\langle \psi_m{}^0 \,|\, \sum_i Q_i x_i \,|\, \psi_n{}^0 \right\rangle \left[\frac{e^{i\left(\omega_{nm}+\omega\right)t'}-1}{\omega_{nm}+\omega} - \frac{e^{i\left(\omega_{nm}-\omega\right)t'}-1}{\omega_{nm}-\omega}\right]$$

$\left|b_m\left(t'\right)\right|^2$ = probability of trans from state from *n* to *m*.

Transitions are peaked at

$\omega = \omega_{nm}$, and $\omega = -\omega_{nm}$