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Perturbation treatment of the first excited states of He

$$E^{(0)} = -\frac{5Z^2}{8}\left(\frac{e^2}{4\pi\varepsilon_0 a_0}\right) = -68.03\ eV$$

n=2 hydrogenlike is fourfold degenerate $2s + 2p_x + 2p_y + 2p_z$ same energy

first excited unperturbed energy level of He is eightfold degenerate

$\psi_1^{(0)} = 1s(1)2s(2)$ $\psi_2^{(0)} = 2s(1)1s(2)$ $\psi_3^{(0)} = 1s(1)2p_x(2)$ $\psi_4^{(0)} = 2p_x(1)1s(2)$

$\psi_5^{(0)} = 1s(1)2p_y(2)$ $\psi_6^{(0)} = 2p_y(1)1s(2)$ $\psi_7^{(0)} = 1s(1)2p_z(2)$ $\psi_8^{(0)} = 2p_z(1)1s(2)$

$$2p_z = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} r_1 e^{-Z\frac{r_1}{2a_0}}\cos\theta_1$$

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

secular determinant contain 64 elements $H'_{ij} = H'_{ji}$

$$\Rightarrow \begin{vmatrix} b_{11} & H'_{12} & & & & & & \\ H'_{12} & b_{22} & & & & & & \\ & & b_{33} & H'_{34} & & & & \\ & & H'_{34} & b_{44} & & & & \\ & & & & b_{55} & H'_{56} & & \\ & & & & H'_{56} & b_{66} & & \\ & & & & & & b_{77} & H'_{78} \\ & & & & & & H'_{78} & b_{88} \end{vmatrix} = 0$$

$b_{ii} = H'_{ii} - E^{(1)}$ $i = 1 \sim 8$

the zeroth order functions

$\phi_1^{(0)} = c_1\psi_1^{(0)} + c_2\psi_2^{(0)}$ $\phi_2^{(0)} = \bar{c}_1\psi_1^{(0)} + \bar{c}_2\psi_2^{(0)}$ $\phi_3^{(0)} = c_3\psi_3^{(0)} + c_4\psi_4^{(0)}$

$\phi_4^{(0)} = \bar{c}_3\psi_3^{(0)} + \bar{c}_4\psi_4^{(0)}$ $\phi_5^{(0)} = c_5\psi_5^{(0)} + c_6\psi_6^{(0)}$ $\phi_6^{(0)} = \bar{c}_5\psi_5^{(0)} + \bar{c}_6\psi_6^{(0)}$

$\phi_7^{(0)} = c_7\psi_7^{(0)} + c_8\psi_8^{(0)}$ $\phi_8^{(0)} = \bar{c}_7\psi_7^{(0)} + \bar{c}_8\psi_8^{(0)}$

the first determinant

$$\begin{vmatrix} H'_{11} - E^{(1)} & H'_{12} \\ H'_{12} & H'_{22} - E^{(1)} \end{vmatrix} = 0$$

coulomb integral

$$H'_{11} = \iint [1s(1)]^2 [2s(2)]^2 \frac{e^2}{4\pi\varepsilon_0 r_{12}} d\tau_1 d\tau_2 = H'_{22} = J_{1s2s}$$

$H'_{33} = H'_{44}$ $H'_{55} = H'_{66}$ $H'_{77} = H'_{88}$

$$H'_{12} = K_{1s2s} = \iint 1s(1)2s(2)\frac{e^2}{4\pi\varepsilon_0 r_{12}} 2s(1)1s(2)\, d\tau_1 d\tau_2$$

exchange integral

$$J_{mn} = \langle f_m(1)f_n(2)| \frac{e^2}{4\pi\varepsilon_0 r_{12}} |f_m(1)f_n(2)\rangle$$

$$K_{mn} = \langle f_m(1)f_n(2)| \frac{e^2}{4\pi\varepsilon_0 r_{12}} |f_n(1)f_m(2)\rangle$$

$$\Rightarrow \begin{vmatrix} J_{1s2s} - E^{(1)} & K_{1s2s} \\ K_{1s2s} & J_{1s2s} - E^{(1)} \end{vmatrix} = 0$$

$(J_{1s2s} - E^{(1)})^2 = (K_{1s2s})^2$

$E_1^{(1)} = J_{1s2s} - K_{1s2s}$

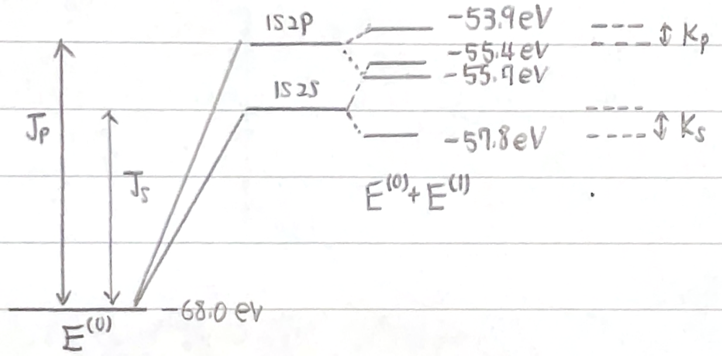
$E_2^{(1)} = J_{1s2s} + K_{1s2s}$

$$c_1 K_{1s2s} + c_2 K_{1s2s} = 0$$
$$c_1 K_{1s2s} + c_2 K_{1s2s} = 0$$
$$\Rightarrow c_2 = -c_1 , \quad \langle \phi_1^{(0)} | \phi_1^{(0)} \rangle = \langle c_1 \psi_1^{(0)} - c_1 \psi_2^{(0)} | c_1 \psi_1^{(0)} - c_1 \psi_2^{(0)} \rangle$$
$$= |c_1|^2 + |c_1|^2 = 1$$
$$\Rightarrow c_1 = \frac{1}{\sqrt{2}}$$

$$\phi_1^{(0)} = \frac{1}{\sqrt{2}}(\psi_1^{(0)} - \psi_2^{(0)}) = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 2s(1)1s(2)\right]$$
$$\phi_2^{(0)} = \frac{1}{\sqrt{2}}(\psi_1^{(0)} + \psi_2^{(0)}) = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) + 2s(1)1s(2)\right]$$

⋮

$$J_{1s2s} = \frac{17}{81}\frac{Ze^2}{4\pi\varepsilon_0 a_0} = 11.42\,eV \qquad J_{1s2p} = \frac{59}{243}\frac{Ze^2}{4\pi\varepsilon_0 a_0} = 13.21\,eV$$
$$K_{1s2s} = \frac{16}{729}\frac{Ze^2}{4\pi\varepsilon_0 a_0} = 1.19\,eV \qquad K_{1s2p} = \frac{112}{6561}\frac{Ze^2}{4\pi\varepsilon_0 a_0} = 0.93\,eV$$



$$E^{(0)} + E_4^{(1)} = E^{(0)} + J_{1s2p} + K_{1s2p}$$
$$E^{(0)} + E_2^{(1)} = E^{(0)} + J_{1s2s} + K_{1s2s}$$
$$E^{(0)} + E_3^{(1)} = E^{(0)} + J_{1s2p} - K_{1s2p}$$
$$E^{(0)} + E_1^{(1)} = E^{(0)} + J_{1s2s} - K_{1s2s}$$

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Time-dependent perturbation theory

$$\hat{H}^0\psi_k^0 = E_k^0\psi_k^0$$

$$-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = (\hat{H}^0+\hat{H}')\Psi$$

$$-\frac{\hbar}{i}\frac{\partial\Psi^0}{\partial t} = \hat{H}^0\Psi^0 \qquad \Psi_k^0 = e^{-iE_k^0\frac{t}{\hbar}}\psi_k^0$$

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

$$\Psi = \sum_k b_k\Psi_k^0 = \sum_k b_k(t)e^{-iE_k^0\frac{t}{\hbar}}\psi_k^0$$

$$\Rightarrow -\frac{\hbar}{i}\sum_k\frac{db_k}{dt}e^{-iE_k^0\frac{t}{\hbar}}\psi_k^0 + \sum_k E_k^0 b_k e^{-iE_k^0 t\frac{1}{\hbar}}\psi_k^0 = \sum_k b_k e^{-iE_k^0\frac{t}{\hbar}}E_k^0\psi_k^0 + \sum_k b_k e^{-iE_k^0\frac{t}{\hbar}}\hat{H}'\psi_k^0$$

$$-\frac{\hbar}{i}\sum_k\frac{db_k}{dt}e^{-iE_k^0\frac{t}{\hbar}}\psi_k^0 = \sum_k b_k e^{-iE_k^0\frac{t}{\hbar}}\hat{H}'\psi_k^0$$

$\times\psi_m^{0*}$

$$-\frac{\hbar}{i}\sum_k\frac{db_k}{dt}e^{-iE_k^0\frac{t}{\hbar}}\delta_{mk} = \sum_k b_k e^{-iE_k^0\frac{t}{\hbar}}\langle\psi_m^0|\hat{H}'|\psi_k^0\rangle$$

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

$t=0$, $\Psi = e^{-iE_n^0\frac{t}{\hbar}}\psi_n^0$

$\Rightarrow b_n(0)=1$, $b_k(0)=0$ for $k\neq n$
$=\delta_{kn}$

assume $\hat{H}'$ is small and acts for only a short time

$$\frac{db_m}{dt} \approx -\frac{i}{\hbar}e^{i(E_m^0-E_n^0)\frac{t}{\hbar}}\langle\psi_m^0|\hat{H}'|\psi_n^0\rangle$$

$$b_m(t') \cong \delta_{mn} - \frac{i}{\hbar}\int_0^{t'} e^{i(E_m^0-E_n^0)\frac{t}{\hbar}}\langle\psi_m^0|\hat{H}'|\psi_n^0\rangle dt$$

$$\Psi = \sum_m b_m(t')e^{-iE_m^0\frac{t}{\hbar}}\psi_m^0 \quad \text{for } t\geq t'$$

$$b_k(t) = b_k^0(t) + \lambda b_k^{(1)}(t) + \lambda^2 b_k^{(2)}(t) + \cdots$$

$$\frac{db_k^0(t)}{dt} + \lambda\frac{db_k^{(1)}(t)}{dt} + \cdots = -\frac{i}{\hbar}\sum_k\left[b_k^0(t)+\lambda b_k^{(1)}(t)+\cdots\right]e^{i\frac{E_m^0-E_k^0}{\hbar}t}\ \lambda\langle\psi_m^0|\lambda\hat{H}'|\psi_k^0\rangle$$

$$\lambda^0 \Rightarrow \frac{db_k^{(0)}(t)}{dt} = 0 \qquad \Rightarrow b_k^{(0)}(t) = \text{constant}$$

$$\lambda^1 \Rightarrow \frac{db_k^{(1)}(t)}{dt} = -\frac{i}{\hbar}\sum_k c_k^{(0)}\langle\psi_m^0|\hat{H}'|\psi_k^0\rangle e^{i\frac{E_m^0-E_k^0}{\hbar}t} \quad \text{—— (A)}$$

$$\lambda^2 \Rightarrow \frac{db_k^{(2)}(t)}{dt} = -\frac{i}{\hbar}\sum_k c_k^{(0)}\langle\psi_m^0|\hat{H}'|\psi_k^0\rangle e^{i\frac{E_m^0-E_k^0}{\hbar}t}$$

$$(A) = -\frac{i}{\hbar}\sum_k\delta_{ki}\langle\psi_m^0|\hat{H}'|\psi_n^0\rangle e^{i\omega t} = -\frac{i}{\hbar}\langle\psi_m^0|\hat{H}'|\psi_n^0\rangle e^{i\omega t}, \quad \int\frac{db_k^{(1)}(t)}{dt}dt = \int -\frac{i}{\hbar}\langle\psi_m^0|\hat{H}'|\psi_n^0\rangle e^{i\omega t}dt$$

$$b_k^{(1)}(t) - b_k^{(1)}(0) = -\frac{i}{\hbar}\cdots, \quad b_m^{(1)}(t) = -\frac{i}{\hbar}\int\langle\psi_m^0|\hat{H}'|\psi_n^0\rangle dt\, e^{i\omega t}$$

then $\quad b_k(t) \cong b_k^{(0)}(t) + \lambda b_k^{(1)}(t) = \delta_{ki} + \lambda b_k^{(1)}(t)$

$$|\psi(r,t)\rangle = \sum_k b_k(t)|\psi_k(t)\rangle e^{-i\frac{E_k}{\hbar}t} = \sum_k(\delta_{ki}+\lambda b_k^{(1)}(t))|\psi_k(t)\rangle e^{-i\frac{E_k}{\hbar}t}$$

$$= |\psi_i(r)\rangle e^{-\frac{E_i}{\hbar}it} + \sum\lambda b_k^{(1)}(t)|\psi_k(r)\rangle e^{-i\frac{E_k}{\hbar}t}$$

Ex: $\lambda \hat{H}' = B\cos(\omega t)$ $\quad P(|\psi_i\rangle \to |\psi_f\rangle) = ?$

$$P_{if}(t) = |\langle \psi_f(r)|\psi(r,t)\rangle|^2 = \left|\overset{0}{\langle \psi_f|\psi_i\rangle} e^{-\frac{E_i}{\hbar}ti} + \sum_{k\neq i} \lambda b_k^{(1)} \langle \psi_f|\psi_k\rangle e^{-i\frac{E_k}{\hbar}t}\right|^2 = |\lambda b_k^{(1)}|^2$$

$$= \left|\frac{1}{\hbar}\int_0^t \langle \psi_f|\lambda \hat{H}'|\psi_i\rangle e^{i\omega t} dt\right|^2$$

$$= \frac{1}{\hbar^2}\left|\int_0^t B\cos\omega t \,\rangle e^{i\omega t} dt\right|^2 = \frac{\langle \psi_f|B|\psi_i\rangle^2}{\hbar^2}\left|\int_0^t \frac{e^{i\omega t}+e^{-i\omega t}}{2i} e^{i\omega_{fi}t} dt\right|^2$$

$$= \frac{\langle \psi_f|B|\psi_i\rangle^2}{4\hbar^2}\left|\int_0^t e^{i(\omega_{fi}+\omega)t} + e^{i(\omega_{fi}-\omega)t} dt\right|^2$$

$$= \frac{\langle \psi_f|B|\psi_i\rangle^2}{4\hbar^2}\left[\frac{e^{i(\omega_{fi}+\omega)t}}{i(\omega_{fi}+\omega)}\Bigg|_0^t - \frac{e^{i(\omega_{fi}-\omega)t}}{i(\omega_{fi}-\omega)}\Bigg|_0^t\right]^2$$

$$= \frac{\langle \psi_f|B|\psi_i\rangle^2}{4\hbar^2}\left|\frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega_{fi}+\omega} - \frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega}\right|^2$$

$$= \frac{\langle \psi_f|B|\psi_i\rangle^2}{4\hbar^2}\left|e^{i\frac{(\omega_{fi}+\omega)t}{2}} \frac{\sin(\frac{\omega_{fi}+\omega}{2}t)}{\omega_{fi}+\omega} + e^{i\frac{\omega_{fi}-\omega}{2}t} \frac{\sin(\frac{\omega_{fi}-\omega}{2}t)}{\omega_{fi}-\omega}\right|^2 \quad -(B)$$

if $\omega = 0$, $(B) = \dfrac{\langle \psi_f|B|\psi_i\rangle^2}{\hbar^2}\left|\dfrac{\sin\frac{\omega_{fi}t}{2}}{\frac{\omega_{fi}}{2}}\right|^2$

when $\omega \sim \omega_{fi}$, the first term of (B) can be inglected

$$(B) = \frac{\langle \psi_f|B|\psi_i\rangle^2}{(\omega_{fi}-\omega)^2\hbar^2} \sin^2\left[\frac{(\omega_{fi}-\omega)t}{2}\right] \quad \text{resonance absorption}$$

when $\omega \sim -\omega_{fi}$, the second term of (B) can be inglected

$$(B) = \frac{\langle \psi_f|B|\psi_i\rangle^2}{(\omega_{fi}+\omega)^2\hbar^2} \sin^2\left[\frac{(\omega_{fi}+\omega)t}{2}\right] \quad \text{induce emission} \Rightarrow \text{laser}$$

$\Delta N = dN = \rho(E_f)\, dE_f$

$$P_{if}' = \sum P_{if}\,\Delta N = \int P_{if}\, dN = \int_{E_f-\Delta}^{E_f+\Delta} P_{if}\, \rho(E_f)\, dE_f$$

if $\omega = 0$, $\quad \overline{P}_{if} = \displaystyle\int_{E_f-\Delta}^{E_f+\Delta} \frac{\langle \psi_f|B|\psi_i\rangle^2}{\hbar^2}\left|\frac{\sin(\frac{\omega_{fi}t}{2})}{\frac{\omega_{fi}}{2}}\right|^2 \rho(E_f)\, dE_f$

$$= \frac{2t}{\hbar}\langle \psi_f|B|\psi_i\rangle^2 \rho(E_f) \underbrace{\int_{-\delta}^{\delta}\frac{\sin^2\beta}{\beta^2}d\beta}_{\approx\pi} \qquad \beta = \frac{\omega_{fi}t}{2}, \quad \pm\delta = \frac{(E_f - E_i \pm \Delta)t}{2\hbar}$$

$$= \frac{2\pi t}{\hbar}\langle \psi_f|B|\psi_i\rangle^2 \rho(E_f)$$

$$W_{if} = \frac{d\overline{P}_{if}}{dt} = \frac{2\pi}{\hbar}\langle \psi_f|B|\psi_i\rangle^2 \rho(E_f) \quad \text{Fermi gold rule}$$

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a ground state of H at par cap. when $t\geq 0$, $\vec{E}=E_0 e^{-\frac{t}{\tau}}\hat{z}$, $P(2S\leftrightarrow 2P)$?

$$\langle\psi_i|\lambda\hat{H}'|\psi_f\rangle = -\vec{\mu}\cdot\vec{E} = e\vec{r}\cdot\vec{E} = eE_0 z e^{-\frac{t}{\tau}}$$

$$P_{if} = \left|\frac{1}{i\hbar}\int_0^t \langle\psi_f|\lambda\hat{H}'|\psi_f\rangle e^{i\omega_{fi}t}dt\right|^2 = \left|\frac{\langle\psi_f|E_0 z|\psi_i\rangle}{\hbar}\underline{\underline{\int_0^t e^{(-\frac{1}{\tau}+i\omega_{fi})t}dt}}\right|^2$$ let $C=-\frac{1}{\tau}+i\omega_{21}$

$$=\frac{1}{C}\int_0^t e^{Ct}d(Ct)$$

$$=\frac{1}{-\frac{1}{\tau}+i\omega_{21}}\left[e^{(-\frac{1}{\tau}+i\omega_{21})t}-1\right]$$

$$\langle 200|eE_0 z|100\rangle = eE_0\int \psi_{200}^* z\,\psi_{100}\,d^3\vec{r}$$
$$= eE_0\int \psi_{200}^* r\cos\theta\,\psi_{100}\,d^3\vec{r}$$
$$= eE_0\int_0^\infty R_{20}^* R_{10} r^3 dr\int Y_0^{0*}\cos\theta\, Y_0^0\, d\Omega = 0$$

similarly, $\langle 211|eE_0 z|100\rangle = \langle 21,-1|eE_0 z|100\rangle = 0$

$$\langle 210|eE_0 z|100\rangle = eE_0\int \psi_{210}^* r\cos\theta\,\psi_{100}\,d^3\vec{r} = eE_0\int_0^\infty R_{21}^* R_{10}\int Y_1^{0*}\cos\theta\, Y_0^0\, d\Omega$$
$$= \frac{eE_0}{4\sqrt{2}\pi a_0^4}\int_0^\infty e^{-\frac{r}{2a_0}} e^{-\frac{r}{a_0}} r^4 dr\int \cos^2\theta\sin\theta\, d\theta\, d\varphi$$
$$= \frac{eE_0}{4\sqrt{2}\pi a_0^4}\int_0^\infty r^4 e^{-\frac{3r}{2a_0}}dr\int_0^{2\pi}d\varphi\int_0^{\pi}\cos^2\theta\, d(\cos\theta)$$
$$= \frac{e}{4\sqrt{2}\pi a_0^4}\left(\frac{4}{3}\right)^4 a_0^5\, 2\pi\frac{2}{3} = \frac{1}{4\sqrt{2}}\left(\frac{4}{3}\right)^5 a_0 eE_0$$

$$\Rightarrow P_{if} = \left|\frac{\langle\psi_f|eE_0 z|\psi_i\rangle}{\hbar}\int_0^t e^{(-\frac{1}{\tau}+i\omega_{fi})t}dt\right|^2 = \frac{1}{32}\left(\frac{4}{3}\right)^{10}\frac{a_0^2 e^2 E_0^2\tau^2}{\hbar^2}\,\frac{1+e^{-\frac{2t}{\tau}}-2e^{-\frac{t}{\tau}}\cos\omega_{21}t}{1+\tau^2\omega_{21}^2}$$

only $|100\rangle\leftrightarrow|210\rangle$ can happened $\rightarrow$ selective rule $\Delta l=\pm 1$ $\Delta m_l=0$