Hamiltonian off diagonal term

Consider the time dependent Schrodinger EQ for two state system $|1\rangle$ and $|2\rangle$ off diagonal terms represent coupling a interaction of quantum states, these terms are responsible for transitions and exchange of probability amplitudes between the states

Show that if matrix is diagonal $\Rightarrow$ wavefunction in orbital $|1\rangle$ would stay there all the time, off diagonal term leads to oscillation between two orbitals

example of a two state system is the spin of an electron $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$

Time-dependent Schrodinger Equation:

dot product
$\langle A|B\rangle = A_1^* B_1 + A_2^* B_2 \ldots$

$$i\hbar \frac{d}{dt}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle$$

Given the two states of the system are $|1\rangle$ and $|2\rangle$ a general state is linear combination

in $\mathbb{C}^n$ but $|\,\rangle$ is column vector then $\langle\,|$ is row vector

$|\psi\rangle = c_1|1\rangle + c_2|2\rangle$ ... c_1, c_2 probability amplitude

Basis states are orthonormal $\langle i|j\rangle = \delta_{ij} \Rightarrow c_i = \langle i|\psi\rangle$

c_1, c_2 can be considered coordinates in complex Hilbert space

if $|\psi\rangle$ normalized norm is unity

$$|\psi\rangle = \begin{pmatrix}\langle 1|\psi\rangle \\ \langle 2|\psi\rangle\end{pmatrix} = \begin{pmatrix}c_1 \\ c_2\end{pmatrix} = c_1\begin{pmatrix}1\\0\end{pmatrix} + c_2\begin{pmatrix}0\\1\end{pmatrix}$$

$|c_1|^2 + |c_2|^2 = 1$

δ_{ij}

Basis states correspond to basis vectors
$$|1\rangle = \begin{pmatrix}\langle 1|1\rangle \\ \langle 2|1\rangle\end{pmatrix} = \begin{pmatrix}1\\0\end{pmatrix}$$
$$|2\rangle = \begin{pmatrix}\langle 1|2\rangle \\ \langle 2|2\rangle\end{pmatrix} = \begin{pmatrix}0\\1\end{pmatrix}$$

Operator Hermitian $\Leftrightarrow \langle i|H|j\rangle = \langle j|H|i\rangle^*$

Observable quantities related to hermitian operators $H_{ij} = \langle i|H|j\rangle = \langle j|H|i\rangle^*$

Produce 2×2 matrix $H = \begin{pmatrix}\langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle\end{pmatrix}$

for time independent SG $\begin{pmatrix}H_{11} & H_{12} \\ H_{21} & H_{22}\end{pmatrix}\begin{pmatrix}c_1\\c_2\end{pmatrix} = E\begin{pmatrix}c_1\\c_2\end{pmatrix}$

Approach: Consider time dependent SG: $i\hbar\frac{d}{dt}\Psi(t) = H\Psi(t)$

the wave function can be written $\Psi(t) = c_1(t)|1\rangle + c_2(t)|2\rangle$ where $c_1(t), c_2(t)$ are time dependent probability amplitudes

Given the general Hamiltonian matrix for a two state system

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{pmatrix} = \begin{pmatrix} \langle 1|H|1\rangle & \langle 1|H|2\rangle \\ \langle 2|H|1\rangle & \langle 2|H|2\rangle \end{pmatrix}$$

- Given the off-diagonal elements are zero $\Rightarrow$ $H = \begin{pmatrix} H_{11} & 0 \\ 0 & H_{22} \end{pmatrix}$

write the schrödinger equation for $|\psi\rangle = c_1(t)|1\rangle + c_2(t)|2\rangle$

two equations $i\hbar \frac{d}{dt} c_1(t) = H_{11} c_1(t)$ $\Leftrightarrow$ $\frac{d}{dt} c_1(t) = \frac{H_{11} c_1(t)}{i\hbar}$

$i\hbar \frac{d}{dt} c_2(t) = H_{22} c_2(t)$ $\Leftrightarrow$ $\int \frac{1}{c_1(t)} dc_1(t) = \frac{H_{11}}{i\hbar} \int 1 \, dt$

Partial differential equations $\approx$ separation of variables $\Leftrightarrow$ $\ln|c_1(t)| = \frac{H_{11}}{i\hbar} t$

Given now the system starts in $|1\rangle$ $\Rightarrow$ $c_1(0) = 1$ $c_2(0) = 0$ $\Leftrightarrow$ Solution $c_1(t) = c_1(0)\, e^{-\frac{i}{\hbar} H_{11} t}$

and $c_2(t) = c_2(0)\, e^{-i/\hbar\, H_{11} t}$

$\psi(t) = e^{-i/\hbar\, H_{11}(t)} |1\rangle$ remain in this state for infinity

Given now the off diagonal elements are not zero

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \Rightarrow SG: \quad \begin{aligned} i\hbar \frac{d}{dt} c_1(t) &= H_{11} c(t) + H_{12} c_2(t) \\ i\hbar \frac{d}{dt} c_2(t) &= H_{21} c_1(t) + H_{22} c_2(t) \end{aligned}$$

as Ψ can be formulated as coordinates in Hilbert space $|\psi(t)\rangle = \begin{pmatrix} \langle 1|\psi(t)\rangle \\ \langle 2|\psi(t)\rangle \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$

Betrachte $H_{11}, H_{22} = 0$ let $H_{12} = H_{21} = V$ where V represents coupling

$$i\hbar \frac{d}{dt} c_1(t) = V c_2(t)$$

$$i\hbar \frac{d}{dt} c_2(t) = V c_1(t)$$

$$\frac{d^2}{dt^2} c_1(t) = -\frac{V^2}{\hbar^2} c_1(t)$$

some kind of harmonic oscillator cant solve this maybe after i finish Analysis III

$\Rightarrow$ derivative $i\hbar \frac{d^2}{dt^2} c_1(t) = V \frac{d}{dt} c_2(t)$

$\Rightarrow$ Substitution $i\hbar \frac{d^2}{dt^2} c_1(t) = V\left(\frac{V}{i\hbar} c_1(t)\right)$

$\hookrightarrow$ But because its a harmonic oscillator we see that we can change states

Simplified Model of Metal bonding

Assume one valence electron is confined in cube with length D, potential in cube is constant

≈ particle in the box, infinite potential outside

a) Determine kinetic energy for the electron for the single atom, and for the solid

Atoms: ⇒ Particle in a box $E_n = \frac{n^2 h^2}{8mD}$ ⇒ Electron will occupy lowest level $E = \frac{h^2}{8mD}$

n... quantum number

m... mass of the electron

D... length of the box

Kinetic energy for solid ⇒ Pauli Principle each electron at position x must occupy unique quantum state

⇒ quantum states according to the band structure

1D chain: • Each state has two electrons ⇒ Spin functions α, β $\uparrow \downarrow$

• System grows ⇒ quasi - continuous

I think the Fermi Energy gives the energy: $E_F \approx \frac{h^2}{8mD^2}\left(\frac{N}{L}\right)^2$

b) Consider two valence electrons per atom and calculate the energy

?? Pauli ⇒ Both valence electrons can occupy lowest energy state $E = \frac{h^2}{8mD^2}$

just take it two times then we are good ?