Tutorial 4

Symmetric states

Q2) Bosons

(a) Photons (bosons) $\{|H\rangle, |V\rangle\}$

3 photons.

$|H\rangle \otimes |H\rangle \otimes |H\rangle \equiv |H\,H\,H\rangle$

$|V\rangle \otimes |V\rangle \otimes |V\rangle \equiv |V\,V\,V\rangle$

$\frac{1}{\sqrt{3}}(|HHV\rangle + |HVH\rangle + |VHH\rangle)$

$\frac{1}{\sqrt{3}}(|VVH\rangle + |VHV\rangle + |HVV\rangle)$

(b) Dim = 4.

2. Fermions. ← Antisymmetric state.

(c) Two e^- in the same position.

$|\phi\rangle \otimes |\phi\rangle$ ← spatial part.

∴ spin part. ⇒ Antisymmetric

$|\chi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ only

Dim = 1

(d) Three e^- in the same position

$|\phi\rangle|\phi\rangle|\phi\rangle$

Dim = 0 because of Pauli's exclusion principle.

3) Variational principle applied to the ground state of He atom.

(b) Error = 2%.

⇓

trial wavefunction is not too bad.

trial wavefunction

$\psi(\vec{r}_1, \vec{r}_2) = \psi_{1s}^{Z}(\vec{r}_1)\,\psi_{1s}^{Z}(\vec{r}_2)$

optimize Z.

$\langle\psi|H|\psi\rangle$ and find

(c) How about for the Fe atom?

Can we use $\psi(\vec{r}_1, \ldots, \vec{r}_N) = \prod_i \psi_i(\vec{r}_i)$

Fe : $[Ar]\,3d^6\,4s^2$.

⥮ ↿ ↿ ↿ ↿

(large errors from exchange energy – not tested)

Need to impose antisymmetry of the entire wavefunction.

Quiz 4.

Time independent perturbation theory ; non-degenerate case :

Sign of $E_n^{(2)}$ for $E_n^{(0)}$ being the ground state energy of H_0.

$$H = H_0 + V$$

$E_n^{(2)}$ for the ground state is < 0.

Variational principle.

For given H, $\langle\psi|H|\psi\rangle \geq E_{g.s.}$ for any $|\psi\rangle$ in the Hilbert space.

g.s. = Ground state

In perturbation theory, the higher order corrections you account for, the closer your answer is to the 'true' answer.

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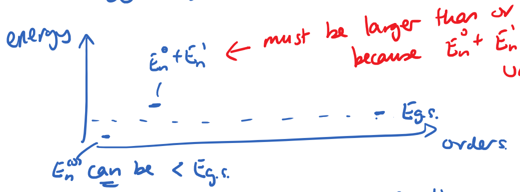
But $E_n^{(1)}$ is not always negative; $E_n^{(1)} = \langle \psi_n^{(0)} | V | \psi_n^{(0)} \rangle$

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

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

True ground state energy $E_{g.s} = \langle \psi_{g.s} | H | \psi_{g.s} \rangle$



$E_n^0 + E_n^1$ ← must be larger than or equal to $E_{g.s.}$, by the variational principle, because $E_n^0 + E_n^1$ is an expectation value of H.

because $E_n^{(0)}$ is an expectation value for H_0, not H.

Degenerate perturbation theory

From W9L2,

we compared coefficients and obtained: state such that $|\psi_n(\lambda)\rangle = |\psi_n^{(0)}\rangle + |\psi_n^{(1)}(\lambda)\rangle + \dots$ varies smoothly with λ and $\to |\psi_n^0\rangle$ when $\lambda \to 0$.

$$\langle \psi_{n_d}^0 | V | \psi_n^0 \rangle = E_n^1 \langle \psi_{n_d}^0 | \psi_n^0 \rangle \quad \text{--- (1)}$$

where $|\psi_{n_d}^0\rangle$ is any state in the degenerate subspace.

Eq (1) tells us that

$$V|\psi_n^0\rangle = E_n^1 |\psi_n^0\rangle \text{ in the degenerate subspace.}$$

(eg if $x^T A y = 0$ for any x

$\Rightarrow A y = 0$

if $x^T A y = 0$ for any x in a subspace W,

$\Rightarrow Ay = 0$ in W.)

$\langle \psi_{n_d}^0 | V - E_n^1 \mathbb{1} | \psi_n^0 \rangle = 0$ for any $|\psi_{n_d}^0\rangle$ in the degenerate subspace.

$\Rightarrow \quad V - E_n^1 \mathbb{1} |\psi_n^0\rangle = 0$ in the degenerate subspace.

So the correct choice of $|\psi_n^0\rangle$ is the eigenstate of V in the degenerate subspace,

and E_n^1 is the corresponding eigenvalue.

What does it mean for $|\psi_n^0\rangle$ to be an eigenvector in the degenerate subspace (W) for V?

$V|\psi_n^0\rangle = E_n^1 |\psi_n^0\rangle$ in W.

Not true that $V|\psi_n^0\rangle = E_n^1 |\psi_n^0\rangle$ in the Hilbert space for $|\psi_n^0\rangle$

$V|\psi_n^0\rangle = E_n^1 |\psi_n^0\rangle + \alpha |\psi_\perp\rangle$

where $|\psi_\perp\rangle$ is orthogonal to the states in W.

Eg matrix V

$$\begin{pmatrix} \overbrace{\begin{matrix} V_{11} & 0 \\ 0 & V_{22} \end{matrix}}^{\text{deg subspace}} & \\ \begin{matrix} \varepsilon_1 & \varepsilon_2 \\ \varepsilon_3 & \varepsilon_4 \end{matrix} & \end{pmatrix}$$

matrix V $\begin{pmatrix} \cdots \\ \varepsilon_1 & \varepsilon_2 \\ \varepsilon_3 & \varepsilon_4 \end{pmatrix}$

$$V\begin{pmatrix}1\\0\\0\\0\end{pmatrix} = \begin{pmatrix}V_{11}\\0\\ \varepsilon_1\\ \varepsilon_3\end{pmatrix}$$

} in the degenerate subspace.

} orthogonal to the degenerate subspace.

In practice, we focus on the degenerate subspace

$\Rightarrow$ submatrix (yellow highlight)

$\rightarrow$ diagonalize it

$\Rightarrow$ eigenvalues are 1st order corrections.

Example.

$$H_0 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad E_1^0 = -1, \; E_2^0 = E_3^0 = 1$$

Corresponding eigenstates are $\{|1\rangle, |2\rangle, |3\rangle\}$
form a basis $\mathcal{B}$.

Consider a perturbation V on H_0.

In the basis $\mathcal{B}$, V is given by

$$V = \begin{pmatrix} 0 & -\varepsilon & 0 \\ -\varepsilon & \boxed{0 & 0} \\ 0 & 0 & 0 \end{pmatrix} \quad \text{where } \varepsilon > 0$$

V_{11}, V_{21}, V_{31}

Find the 1st and 2nd order corrections to the eigenvalue E_1^0 of H_0.

Find the 1st order corrections to E_2^0 and E_3^0.

- Check for degeneracies.

E_1^0 : not degenerate

E_2^0, E_3^0 : degenerate.

$$E_1^1 = \langle 1|V|1\rangle = 0$$

$$E_1^2 = \sum_{m\neq 1} \frac{|\langle \psi_m^0|V|\psi_1^0\rangle|^2}{E_1^0 - E_m^0} = \frac{|V_{21}|^2}{E_1^0 - E_2^0} + \frac{|V_{31}|^2}{E_1^0 - E_3^0}$$

$$= \frac{\varepsilon^2}{-1-1}$$

$$= -\frac{1}{2}\varepsilon^2.$$

If the question says:

Find the ground state eigenvalue of $H = H_0 + V$
to 2nd order in ε.

Need to write: $E_1 = -1 + 0 - \frac{1}{2}\varepsilon^2$

$$= -1 - \frac{1}{2}\varepsilon^2.$$

For E_2^1 and E_3^1, V is already diagonal in the degenerate subspace.

$$E_2^1 = V_{22} = 0$$

$$E_3^1 = V_{33} = 0.$$

Eg. 2D Harmonic Oscillator.

$$\hat{H}_0 = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{m\omega^2}{2}(\hat{x}^2 + \hat{y}^2)$$

$$\hat{x} = \frac{1}{\sqrt{2}\beta}(\hat{a} + \hat{a}^\dagger)$$

$$\hat{y} = \frac{1}{\sqrt{2}\beta}(\hat{b} + \hat{b}^\dagger) \qquad \beta = \sqrt{\frac{m\omega}{\hbar}}.$$

Eigenstates of $\hat{H}_0$ are $\varphi_{np} = \varphi_n(x)\varphi_p(y)$ where $\varphi_n(x)$ and $\varphi_p(y)$

$|n,p\rangle$ are eigenfunctions of the 1D Harmonic oscillator.

$$E_{np} = \hbar\omega(n+\tfrac{1}{2}) + \hbar\omega(p+\tfrac{1}{2})$$
$$= \hbar\omega(n+p+1) \quad , n,p \text{ are non-negative integers.}$$

Consider $V = Kxy$

Use degenerate perturbation theory to find the 1st order corrections to $E_{01} = E_{10}$.

Let's use the basis $\{|1,0\rangle, |0,1\rangle\}$ for our matrix representation of V.

We need to find the matrix

$$\tilde{V} = K \begin{pmatrix} \langle 1,0|xy|1,0\rangle & \langle 1,0|xy|0,1\rangle \\ \langle 0,1|xy|1,0\rangle & \langle 0,1|xy|0,1\rangle \end{pmatrix}$$

$$\hat{x}\hat{y} = \frac{1}{2\beta^2}(\hat{a}+\hat{a}^+)(\hat{b}+\hat{b}^+)$$
$$= \frac{1}{2\beta^2}(\hat{a}\hat{b} + \hat{a}^+\hat{b} + \hat{a}\hat{b}^+ + \hat{a}^+\hat{b}^+)$$

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

$\hat{x}\hat{y}$ is odd and $|1,0\rangle, |0,1\rangle$ have definite parity

$$\langle 1,0|\hat{x}\hat{y}|1,0\rangle = \langle 0,1|\hat{x}\hat{y}|0,1\rangle = 0.$$

$$\langle 1,0|\hat{x}\hat{y}|0,1\rangle = \frac{1}{2\beta^2}\langle 1,0|\hat{a}^+\hat{b}|0,1\rangle$$
$$= \frac{1}{2\beta^2}$$

$$\langle 0,1|\hat{x}\hat{y}|1,0\rangle = \langle 1,0|\hat{x}\hat{y}|0,1\rangle^* = \frac{1}{2\beta^2}$$

So $\tilde{V} = \frac{K}{2\beta^2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

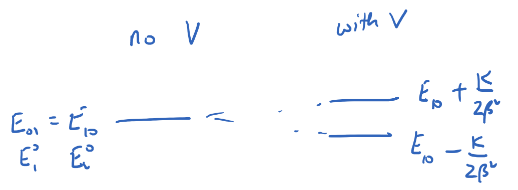
Diagonalize $\tilde{V}$: $\quad \det(\tilde{V} - \lambda I) = 0$

$$\begin{vmatrix} -\lambda & \\ \frac{K}{2\beta^2} & \end{vmatrix} = 0$$

$$\lambda^2 - (K\ ^2 = 0$$

$$\lambda = \pm \frac{K}{2\beta^2}$$

So the 1st order corrections are $E_1' = \frac{K}{2\beta^2}$, $E_2' = -\frac{K}{2\beta^2}$.



degeneracy is broken.

Quiz 5 — folder on CANVAS, Quizzes

Quiz5.pdf.

Hand in 29 Oct in class.
(beginning of class).

(Appendix: 2nd order corrections for degenerate perturbation theory — not tested)

Still with degenerate perturbation theory.

- an approach to find the states that diagonalize V in the degenerate subspace. ("right" basis); or helps us to evaluate the matrix elements for V.

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If we have a Hermitian operator $\hat{P}$ so that $[\hat{P}, \hat{V}] = 0$, and if $|\tilde{\psi}_a^0\rangle$, $|\tilde{\psi}_b^0\rangle$ are eigenstates of $\hat{P}$ with different eigenvalues $P_a \neq P_b$,

then $V_{ab} = \langle \tilde{\psi}_a^0 | V | \tilde{\psi}_b^0 \rangle = 0$

[If $[\hat{P}, \hat{H}_0] = 0$, then $\exists$ a common set of eigenstates for $\hat{P}$ and $\hat{H}_0$.

So we can find eigenstates of $\hat{H}_0$ in the degenerate subspace that diagonalize V.]

Proof: $[\hat{P}, \hat{V}] = 0$.

$$\hat{P}\hat{V}|\tilde{\psi}_b^0\rangle = \hat{V}\hat{P}|\tilde{\psi}_b^0\rangle = P_b \hat{V}|\tilde{\psi}_b^0\rangle$$

Apply $\langle \tilde{\psi}_a^0|$:

LHS: $\langle \tilde{\psi}_a^0 | \hat{P}\hat{V} | \tilde{\psi}_b^0\rangle = P_a \langle \tilde{\psi}_a^0 | \hat{V} | \tilde{\psi}_b^0 \rangle$

RHS: $P_b \langle \tilde{\psi}_a^0 | \hat{V} | \tilde{\psi}_b^0 \rangle$

LHS = RHS $\Rightarrow$ $P_a \langle \tilde{\psi}_a^0 | \hat{V} | \tilde{\psi}_b^0 \rangle = P_b \langle \tilde{\psi}_a^0 | \hat{V} | \tilde{\psi}_b^0 \rangle$

$$(P_a - P_b)\langle \tilde{\psi}_a^0 | \hat{V} | \tilde{\psi}_b^0 \rangle = 0$$

$P_a \neq P_b \Rightarrow \langle \tilde{\psi}_a^0 | \hat{V} | \tilde{\psi}_b^0 \rangle = 0$ //

Example.

Hydrogen atom.

$$H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$$

$H = H_0 + V$, $V = -e|\vec{E}|z$, $|\vec{E}|$ small.

Eigenstates of the hydrogen atom have definite parity.
Degeneracy for E_n is n^2.

(a) What is the 1st order correction to the ground state (1s) eigenvalue of H_0 due to V? $|nlm\rangle = |100\rangle$.

No degeneracy for E_1.

So $E_1^{(1)} = \langle 100 | V | 100 \rangle$
$= 0$ because V is an odd operator, $|100\rangle$ has definite parity.

(b) Show that $[V, L_z] = 0$.

$\vec{L} = \vec{r} \times \vec{p}$

$L_z = r_x p_y - r_y p_x$

$V \propto z$

$[z, L_z] = [z, r_x p_y - r_y p_x] = 0$ because z commutes with x, y, p_x, p_y.

(c) Recall that the 1st excited state of H_0 is degenerate.

The degenerate states are 2s, and three 2p states.

$|2\,0\,0\rangle$ $\quad$ $|2\,1\,-1\rangle$

$|2\,1\,0\rangle$

$|2\,1\,1\rangle$

Using the result in (b) and showing your analysis clearly, find the 1st order corrections to the eigenvalues for the 1st excited state of H_0.

You do not need to evaluate the exact value of the 1st order corrections, if they are non-zero.