Linear Stark effect (conclusion)

Eigenvectors: eigenvalues λ_+ & λ_-

$$\begin{pmatrix} 0-\lambda_+ & -3a_0 \\ -3a_0 & 0-\lambda_+ \end{pmatrix} \overset{u_+}{\begin{pmatrix} C_+ \\ u_+^2 \end{pmatrix}} = 0$$

[i.e. $AX = \lambda X$ then after finding roots $\lambda_1, \ldots \lambda_n$ we look for $X_{(1)} \ldots X_{(n)}$ s.t. $(A - \lambda_1 \mathbb{1}) X_{(1)} = 0$ for λ_1

- Delete one row of $(A - \lambda_1 \mathbb{1})$ matrix, say first
- Then first entry of $X_{(1)}$ vector, say $X_{(1)}^1$, remains undetermined
- Remaining components of $X_{(1)}$ can be determined

~~by~~ in terms of $x'_{(1)} \equiv c_{(1)}$ using remaining rows of $(A - \lambda, \mathbb{1})$ matrix

- Same for each vector $x_{(j)}$
- Normalising $x_{(j)}$ also determines $c_{(j)}$

Using second row above,

$$-3a_0 c_+ - \lambda_+ u_+^2 = -3a_0 c_+ - 3a_0 u_+^2 = 0$$

i.e $u_+^2 = -c_+$; $u_+ = \begin{pmatrix} c_+ \\ -c_+ \end{pmatrix} \longrightarrow \hat{u}_+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

Similarly,

$$-3a_0 c_- - \lambda_- u_-^2 = -3a_0 c_- + 3a_0 u_-^2 = 0$$

i.e $u_-^2 = c_-$ or $\hat{u}_- = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$

Thus, the eigenvectors in D subspace become

$$\psi_+ = \frac{1}{\sqrt{2}}\left(|\overset{n}{2},\overset{\ell}{0},\overset{m}{0}\rangle - |2,1,0\rangle\right)$$

$$\psi_- = \frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right)$$

and their energies are split by $6a_0$

These states do not have fixed parity ... not parity eigenstates because perturbation V breaks parity.

$$\mathcal{P} V \mathcal{P}^\dagger = \mathcal{P} z \mathcal{P}^\dagger = -z$$

Variational method
for bound states

- Make a good guess at possible ground state wavefunction $|\bar{0}\rangle$ of the hamiltonian H
- Calculate $\bar{H} = \dfrac{\langle \bar{0} | H | \bar{0} \rangle}{\langle \bar{0} | \bar{0} \rangle}$

... this itself is a good estimate for E_0 if $|\bar{0}\rangle$ choice was good

In practice we choose a trial function $|\bar{0}; \lambda_1 .. \lambda_p\rangle$ withe undetermined parameters $\lambda_1 .. \lambda_p$

Find an improved estimate for E_0 by setting $\frac{\partial \bar{H}}{\partial \lambda_1} = \frac{\partial \bar{H}}{\partial \lambda_2} = .. = 0$

Note applies to ground state energy only

Theorem : $\bar{H} \geqslant E_0 \rightarrow$ true g.s. energy

Proof: Let trial wave function be written

$$|\bar{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\bar{0}\rangle$$

where $|k\rangle$ are the actual eigenstates

$$\bar{H} = \frac{\displaystyle\sum_{l\&k=0}^{\infty} \langle\bar{0}|l\rangle \overbrace{\langle l|H|k\rangle}^{E_k\delta_{lk}} \langle k|\bar{0}\rangle}{\displaystyle\sum_{l\&k=0}^{\infty} \langle\bar{0}|l\rangle \underbrace{\langle l|k\rangle}_{\delta_{lk}} \langle k|\bar{0}\rangle}$$

$$\bar{H} = \frac{\sum_k |\langle \bar{0} | k \rangle|^2 E_k}{\sum_k |\langle \bar{0} | k \rangle|^2} \qquad \overbrace{E_k - E_0 + E_0}^{\text{replace}}$$

$$= \frac{\sum_k |\langle \bar{0} | k \rangle|^2 (E_k - E_0)}{\sum_k |\langle \bar{0} | k \rangle|^2} + E_0$$

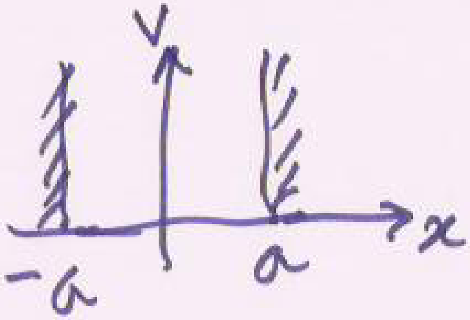
Thus $\bar{H} \geqslant E_0$ .... for g.s. $\because E_k \geqslant E_0$

Equality holds only if $|\bar{0}\rangle$ happens to be exactly the correct $|0\rangle$ QED

This also justifies the variational procedure

Example

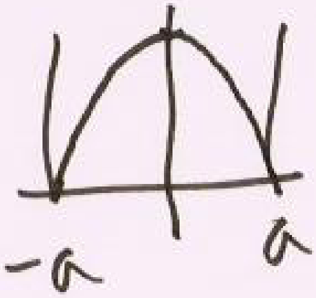
Particle in a box: $|x| < a$



"Good" guess

- Boundary cond.s to be satisfied
- Ground state wave function has no nodes

Suggestion $\langle x|\bar{0}\rangle = \psi_{tr}(x) = -(x^2-a^2)$



$$\bar{H} = \int_{-a}^{a} dx\,(a^2-x^2)\left(-\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2}(a^2-x^2) \Big/ \langle\bar{0}|\bar{0}\rangle$$