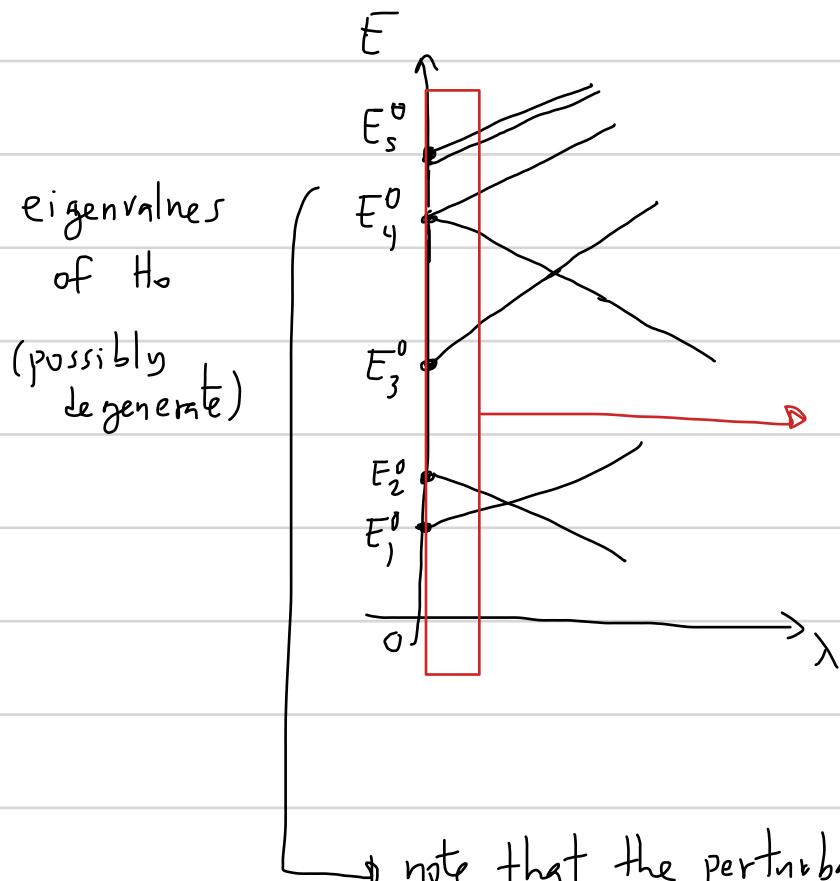


Time-independent Perturbation Theory [CT chap X1, Griffiths 6.1]

Suppose $H = H_0 + H'$, where $H_0 = \sum_n E_n^0 |\Psi_n^0 \rangle \langle \Psi_n^0|$ is a known (solved) nondegenerate Hamiltonian, and H' is a "perturbation", generally $[H_0, H'] \neq 0$.

If H' is "weak" compared to H_0 [more precisely: if the eigenvalues of H' are generally \ll those of H_0] then we can expect H 's eigenspectrum to only change slightly w/ respect to H_0 's one.

Make this systematic: rewrite $H' = \lambda \tilde{H}'$, where \tilde{H}' has eigenvalues "of the same order" as those of H_0 and where λ is an adimensional scaling parameter. Then $H = H_0 + \lambda \tilde{H}'$ and we wish to study what happens to the energies/eigenstates of H as a function of λ , and in particular when $\lambda \ll 1$



general goal of the TIPT that we will develop here: to describe what happens to the energy levels (and eigenstates) in this region where λ is small enough that no 'level crossings' have occurred.

note: understanding these crossings is possible too but requires more sophisticated methods

note that the perturbation may break or 'lift' some degeneracies that occur in the spectrum of H_0 - while other ones may remain.

Note: for simplicity, we only consider here systems where H_0 has a discrete energy spectrum
 the Hilbert space \mathcal{E} can be infinite-dimensional though.

1.1) Case where H_0 is nondegenerate

Expand eigenfunctions/values of $H(\lambda)$ as power series in λ

$$|\psi_n\rangle(\lambda) = |\psi_n^0\rangle + \sum_{j=1}^{\infty} \underbrace{\lambda^j |\tilde{\psi}_n^j\rangle}_{\equiv |\psi_n^j\rangle} \quad E_n(\lambda) = E_n^0 + \sum_{j=1}^{\infty} \underbrace{\lambda^j \tilde{E}_n^j}_{\equiv E_n^j} \xrightarrow{\text{exponent}} \text{note this is an index, not an exponent}$$

Goal: determine systematically, up to some desired order j , the "j-th order corrections"

$$E_n^j \equiv \lambda^j \tilde{E}_n^j \quad \text{and} \quad |\psi_n^j\rangle \equiv \lambda^j |\tilde{\psi}_n^j\rangle \quad \text{to the "unperturbed" values } E_n^0, |\psi_n^0\rangle,$$

Note: the scaling factor λ and the "tilde" energies and states are just calculational devices that help us do this; they will be dropped shortly.

Attention: $|\psi_n\rangle(\lambda)$ is not normalised yet in this expression [it can't be, since $|\psi_n^0\rangle$ is normalized]

Attention: E_n^j and $|\psi_n^j\rangle$ are not generally eigenvalues/states of H' !

Attention: $|\psi_n^j\rangle$ are also generally not normalized (their norms should decrease with j)

Basic idea: write eigenvalue equation for H using the series expansions, then equate terms w/ same power of λ on both sides

$$H|\Psi_n\rangle = E_n |\Psi_n\rangle$$



$$(H_0 + \lambda \tilde{H}') \left(|\Psi_n^0\rangle + \sum_{j=1}^{\infty} \lambda^j |\tilde{\Psi}_n^j\rangle \right) = \left(E_n^0 + \sum_{j=1}^{\infty} \lambda^j \tilde{E}_n^j \right) \left(|\Psi_n^0\rangle + \sum_{j=1}^{\infty} \lambda^j |\tilde{\Psi}_n^j\rangle \right)$$

So far: exact. Now, for each j , equate terms w/ same power λ^j on both sides.

Note that, by incorporating the λ 's back into each 'tilde' term, we can write the resulting equations purely in terms of 'untilded' H' , E_n^j , $|\Psi_n^j\rangle$:

$$0: H_0 |\Psi_n^0\rangle = E_n^0 |\Psi_n^0\rangle \quad [\text{unperturbed solutions}]$$

$$1: H_0 |\Psi_n^1\rangle + H' |\Psi_n^0\rangle = E_n^0 |\Psi_n^1\rangle + E_n^1 |\Psi_n^0\rangle$$

$$2: H_0 |\Psi_n^2\rangle + H' |\Psi_n^1\rangle = E_n^0 |\Psi_n^2\rangle + E_n^1 |\Psi_n^1\rangle + E_n^2 |\Psi_n^0\rangle$$

⋮

$$j: H_0 |\Psi_n^j\rangle + H' |\Psi_n^{j-1}\rangle = E_n^0 |\Psi_n^j\rangle + E_n^1 |\Psi_n^{j-1}\rangle + \dots + E_n^j |\Psi_n^0\rangle$$

now solve iteratively (find $E_n^1, |\Psi_n^1\rangle \rightarrow$ use solutions in eqs for $E_n^2, |\Psi_n^2\rangle$ etc.)

ex: multiplying order 1 eq from left w/ $\langle \Psi_n^0 |$

$$\underbrace{\langle \Psi_n^0 | H_0 | \Psi_n^1 \rangle}_{= E_0 \langle \Psi_n^0 | \Psi_n^1 \rangle} + \langle \Psi_n^0 | H' | \Psi_n^0 \rangle = E_n^0 \cancel{\langle \Psi_n^0 | \Psi_n^1 \rangle} + E_n^1 \cancel{\langle \Psi_n^0 | \Psi_n^0 \rangle}$$

$$\Rightarrow \boxed{E_n^1 = \langle \Psi_n^0 | H' | \Psi_n^0 \rangle} \quad (*) \quad \text{1st order energy correction} \\ (\text{usually quite good!})$$

1st order eigenstate correction

in (1) above, expand $|\Psi_n^1\rangle$ and $H'|\Psi_n^0\rangle$ in the order-0 (unperturbed) basis

$$|\Psi_n^1\rangle = \sum_{m \neq n} c_m^{(n)} |\Psi_m^0\rangle ; \quad (\star\star)$$

note: $m=n$ term can be excluded since it can always be incorporated into the 0^{th} -order state

Now: multiplying the order 1 eq from the left with $\langle \Psi_m^0 |, m \neq n$ and using $(\star\star)$:

$$\begin{aligned} \langle \Psi_m^0 | H_0 | \Psi_n^1 \rangle + \langle \Psi_m^0 | H' | \Psi_n^0 \rangle &= E_n^0 \langle \Psi_m^0 | \Psi_n^1 \rangle + E_n^1 \cancel{\langle \Psi_m^0 | \Psi_n^0 \rangle} \\ \xrightarrow{\underbrace{c_m^{(n)}}} E_m^0 \langle \Psi_m^0 | \Psi_n^1 \rangle + \langle \Psi_m^0 | H' | \Psi_n^0 \rangle &= E_n^0 \underbrace{\langle \Psi_m^0 | \Psi_n^1 \rangle}_{\cancel{E_n^0 - E_m^0}} \end{aligned}$$

$$\xrightarrow{} c_n^{(n)} = \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0}$$

$$\Rightarrow |\Psi_n^1\rangle = \sum_{m \neq n} \frac{\langle \Psi_m^0 | H' | \Psi_n^0 \rangle}{E_n^0 - E_m^0} |\Psi_m^0\rangle$$

[1st order correction to eigenstates]
(usually quite poor...)

Note: because $\langle \Psi_n^1 | \Psi_n^0 \rangle = 0$ (1st order correction is orthogonal to 0th-order state), then the 1st order expansion of $|\Psi_n\rangle$ is normalized up to $O(\lambda^2)$:

$$\langle \Psi_n | \Psi_n \rangle = \left(\langle \Psi_n^0 | + \langle \Psi_n^1 | + O(\lambda^2) \right) \left(|\Psi_n^0\rangle + |\Psi_n^1\rangle + O(\lambda^2) \right) = 1 + \cancel{(\langle \Psi_n^0 | \Psi_n^0 \rangle + \langle \Psi_n^0 | \Psi_n^1 \rangle + \langle \Psi_n^1 | \Psi_n^0 \rangle)} + O(\lambda^2)$$

2nd order energy

$$2: H_0 |\psi_n^2\rangle + H' |\psi_n^1\rangle = E_n^0 |\psi_n^2\rangle + E_n^1 |\psi_n^1\rangle + E_n^2 |\psi_n^0\rangle$$

Once again: taking the product with $\langle \psi_n^0 |$ from the left

$$\cancel{E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle} + \langle \psi_n^0 | H' | \psi_n^1 \rangle = \cancel{E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle} + E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2$$

Replacing the 1st order eigenstate expression

$$E_n^2 = \langle \psi_n^0 | H' \left(\sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} | \psi_m^0 \rangle \right) = \boxed{\sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$$

- Note that (0th-order) levels above (resp.: below) E_n^0 will tend to lower (resp.: raise) the value of E_n^2 . Thus, at this order, levels tend to "repel" each other as a function of λ .
- Note: if the matrix elements of H' ($\langle \psi_m^0 | H' | \psi_n^0 \rangle$), which have physical dimension of energy, are small in magnitude w/ respect to the energy gaps $E_n^0 - E_m^0$ of the unperturbed Hamiltonian, then we can expect the sum itself above to be small w/ respect not only to E_n^0 , but to $E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$. This corroborates the initial idea that, for 'weak' H' , each successive E_n^j should give a smaller correction.

side note: upper bound to 2nd-order energy

It is possible to obtain a rough upper bound to the 2nd-order correction above without having to perform the full sum (which may be too laborious or inconvenient to use)

Def: $\delta E = \min_m |E_n^0 - E_m^0|$ [minimum energy gap between E_n^0 and any other level of the unperturbed Hamiltonian]

$$\text{then: } |E_n^{(2)}| \leq \frac{1}{\delta E} \sum_{m \neq n} |\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2 = \frac{1}{\delta E} \sum_{m \neq n} \langle \psi_n^0 | H' | \psi_m^0 \times \psi_m^0 | H' | \psi_n^0 \rangle$$

$$= \frac{1}{\delta E} \langle \psi_n^0 | H' \sum_{m \neq n} |\psi_m^0 \times \psi_m^0| H' | \psi_n^0 \rangle = \frac{1}{\delta E} \langle \psi_n^0 | H' (1 - |\psi_n^0 \times \psi_n^0|) H' | \psi_n^0 \rangle$$

$$= \frac{1}{\delta E} \left[\langle H'^2 \rangle_{n,0} - \langle H' \rangle_{n,0}^2 \right] = \frac{(\Delta H')_{n,0}^2}{\delta E}$$

$|E_n^{(2)}| \leq \frac{(\Delta H')_{n,0}^2}{\delta E}$

(where $(\Delta H')_{n,0}^2$ is the variance of the perturbation energy on the unperturbed state $|\psi_n^0\rangle$)

i

In principle we can continue this process systematically: knowing the $\{E_n^0\}$ allows us to obtain the 2nd order eigenstate corrections $|\Psi_n^2\rangle$, which then give us the 3rd order energy correction, and so on. The expressions become larger as the order grows - they can be found in the literature (eg. Landau/Lifschitz).

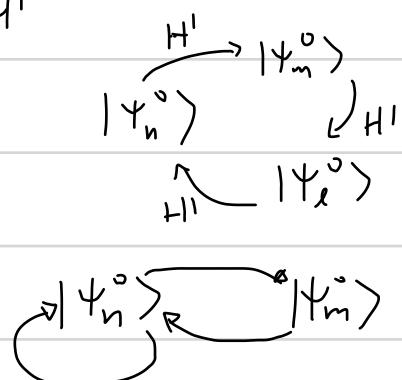
A general feature is that j^{th} -order terms involve j "transition amplitudes" between unperturbed states, each 'mediated' by H'

1st order energies : $\langle \Psi_n^0 | H' | \Psi_n^0 \rangle$ ($|\Psi_n^0\rangle$) $\xrightarrow[H']{} |\Psi_n^0\rangle$

2nd order energies : $\propto \langle \Psi_n^0 | H' | \Psi_m^0 \rangle \langle \Psi_m^0 | H' | \Psi_n^0 \rangle$: $|\Psi_n^0\rangle \xrightarrow[H']{} |\Psi_m^0\rangle$

3rd order energies. $\propto \langle \Psi_n^0 | H' | \Psi_\ell^0 \rangle \langle \Psi_\ell^0 | H' | \Psi_m^0 \rangle \langle \Psi_m^0 | H' | \Psi_n^0 \rangle$
and

$$\langle \Psi_n^0 | H' | \Psi_n^0 \rangle \langle \Psi_n^0 | H' | \Psi_m^0 \rangle \langle \Psi_m^0 | H' | \Psi_n^0 \rangle$$



see eg the wikipedia article on "Perturbation Theory (quantum mechanics)"
for expressions up to 5th order!

Example: 2-level system (eg: double well / Ammonia molecule)
 [cf Feynman ch..., Townsend ch. 11]

This is a system we know how to solve exactly, but it is instructive to compare the exact solution w/ perturbation expansions in different regimes

generic 2-level Hamiltonian is of the form

$$H = \begin{bmatrix} E_0 + \Delta & A \\ A^* & E_0 - \Delta \end{bmatrix}$$

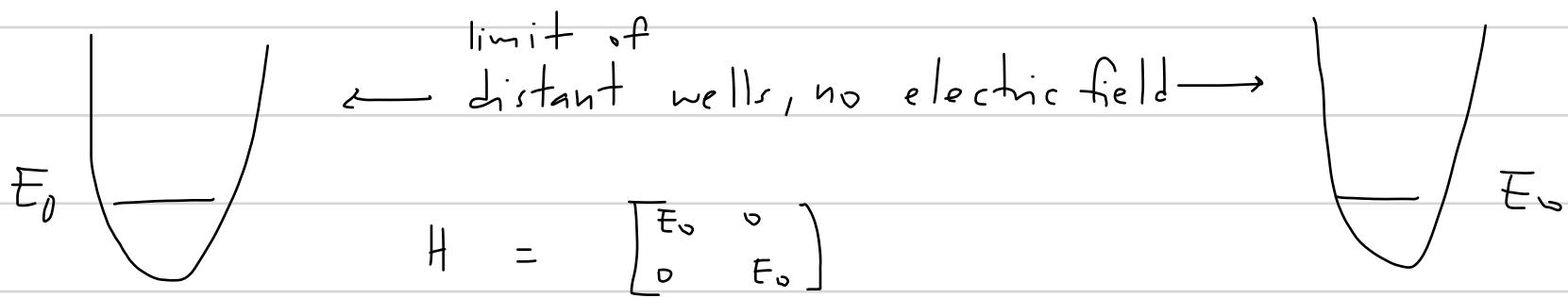
Possible physical interpretation: double well

$E_0 \leftrightarrow$ (ground state) energy for a particle in either individual well

$A \leftrightarrow$ tunneling amplitude between wells

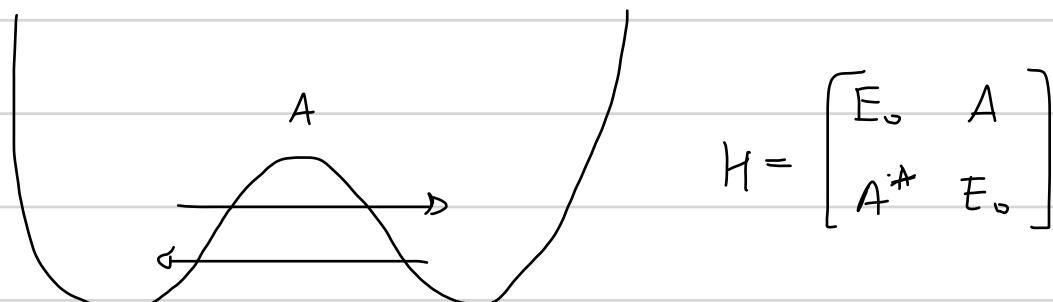
$\Delta \rightarrow$ Asymmetry factor between 2 wells, induced by eg an electric potential gradient [uniform electric field] along the direction linking the wells

$$\Delta = |\vec{d} \cdot \vec{E}|, d = \text{electric dipole}$$



$|L\rangle \leftarrow$ degenerate eigenstates w/ energy $E_0 \rightarrow |R\rangle$
(note all combinations are also eigenstates)

When wells brought close together \rightarrow particle can tunnel between $|L\rangle$ and $|R\rangle$



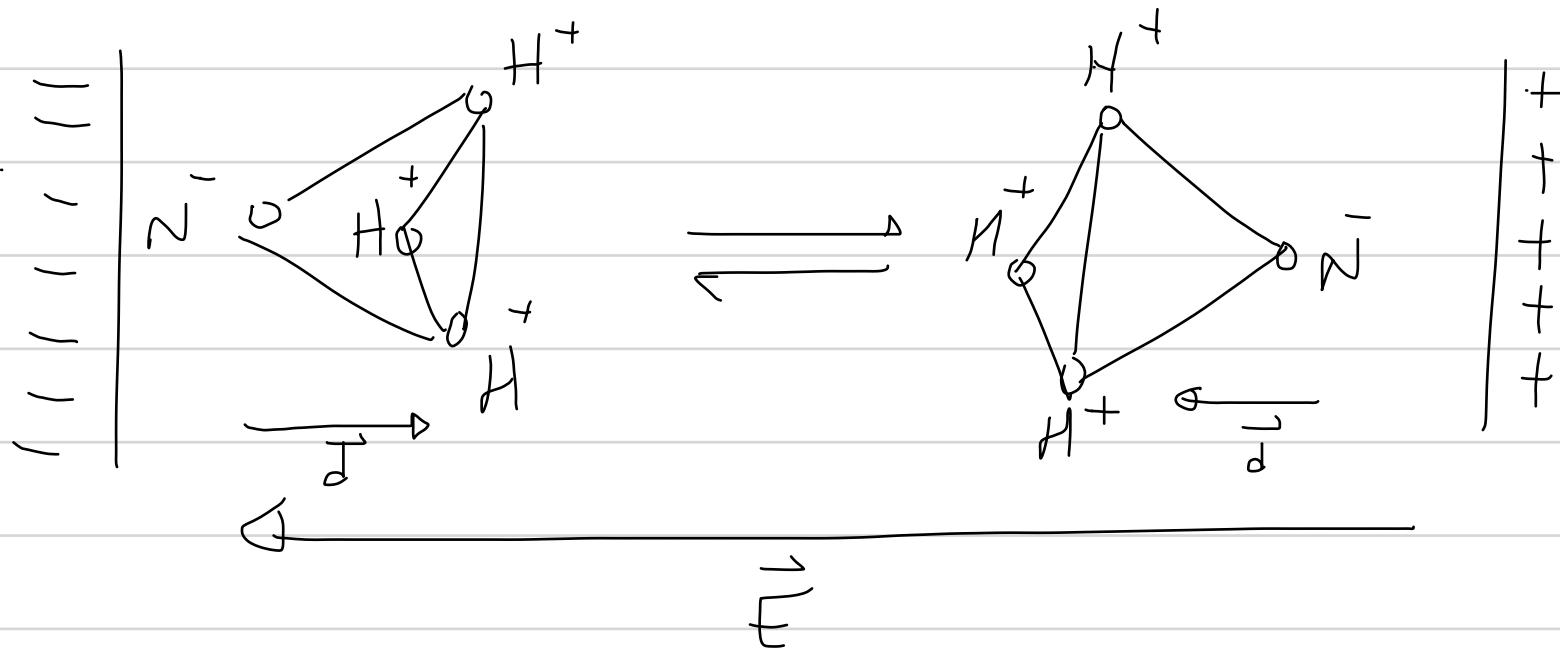
taking A real for simplicity (doesn't change much)

$$H = E_0 \mathbb{1} + A \sigma_x \rightarrow \text{eigenstates are } \frac{1}{\sqrt{2}}[|L\rangle \pm |R\rangle] \Rightarrow E_0 \pm A$$

Adding a potential gradient that 'lifts' L and lowers R side



Specific example: ammonia molecule in electric field



exact eigenvalues : $(E_0 - \lambda + \Delta)(E_0 - \lambda - \Delta) - A^2 = 0 \rightarrow (E_0 - \lambda)^2 - \Delta^2 = A^2$

$$\rightarrow E_0 - \lambda = \pm \sqrt{A^2 + \Delta^2} \rightarrow \boxed{\lambda = E_0 \pm \sqrt{A^2 + \Delta^2} \equiv E_{\pm A}}$$

If $\Delta = 0$ ($\leftrightarrow \vec{E} = 0$) , then $E_s = E_0 \pm A \equiv E_{\pm A}$ as previously

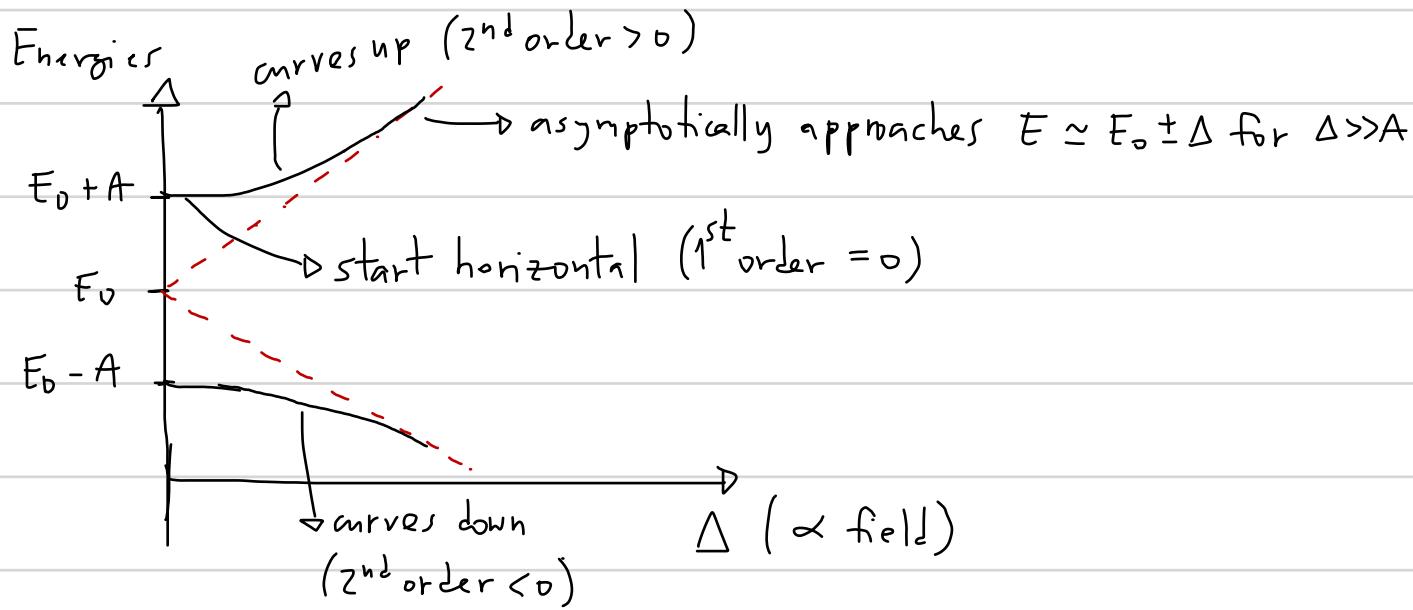
Perturbation Theory Analysis

IF electric field is weak ($\frac{\Delta}{A} \ll 1$) , we can also treat the asymmetry terms as a perturbation $[H = H_0 + H^1 ; H_0 = \begin{bmatrix} E_0 & A \\ A & E_0 \end{bmatrix} ; H^1 = \begin{bmatrix} \Delta & 0 \\ 0 & -\Delta \end{bmatrix} = \Delta \cdot \Gamma_2]$

$$\Rightarrow \boxed{E_{\pm A}^1 = \langle \Psi_{\pm A} | H^1 | \Psi_{\pm A} \rangle = 0} \quad (\langle \pm_x | \sigma_z | \pm_n \rangle)$$

2nd order is lowest nontrivial correction

$$\boxed{E_{\pm A}^2 = \frac{|\langle \Psi_{\pm A} | H^1 | \Psi_{\pm A} \rangle|^2}{E_{\pm A} - E_{\mp A}} = \frac{\Delta^2 \left[\frac{1}{\sqrt{2}} (1, -1) \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \frac{1}{\sqrt{2}} (1) \right]^2}{\pm 2A} = \pm \frac{\Delta^2}{2A}}$$



Comparing w) exact result : $E_{\frac{A}{2}} = E_0 \pm A \sqrt{1 + \underbrace{\frac{\Delta^2}{A^2}}_{= \epsilon}} = E_0 + A \left(1 + \frac{\epsilon}{2} - \frac{\epsilon^2}{4} + \dots\right)$

1st correction (OK!)

$$= E_0 \pm \left(A + \frac{\Delta^2}{2A} - \frac{\Delta^4}{4A^3} + \dots\right)$$

Strong field limit : $\Delta \gg A$

In this case we can take $H_0 = \begin{bmatrix} E_0 + A & 0 \\ 0 & E_0 - A \end{bmatrix}$; $H' = \begin{bmatrix} 0 & A \\ A & 0 \end{bmatrix}$

unperturbed eigenstates : $|L\rangle, |R\rangle$, energies $E_0 \pm \Delta \equiv E_{\frac{L}{R}}$

1st order correction :

$$E_L' = \langle L | H' | L \rangle = A \langle \pm | \sigma_x | \pm \rangle = 0$$

2nd order correction = $E_L'' = \frac{|\langle L | H' | L \rangle|^2}{E_L^0 - E_R^0} = \pm \frac{A^2}{2\Delta}$

$$\rightarrow E_L \approx E_0 \pm \Delta \pm \frac{A^2}{2\Delta}$$

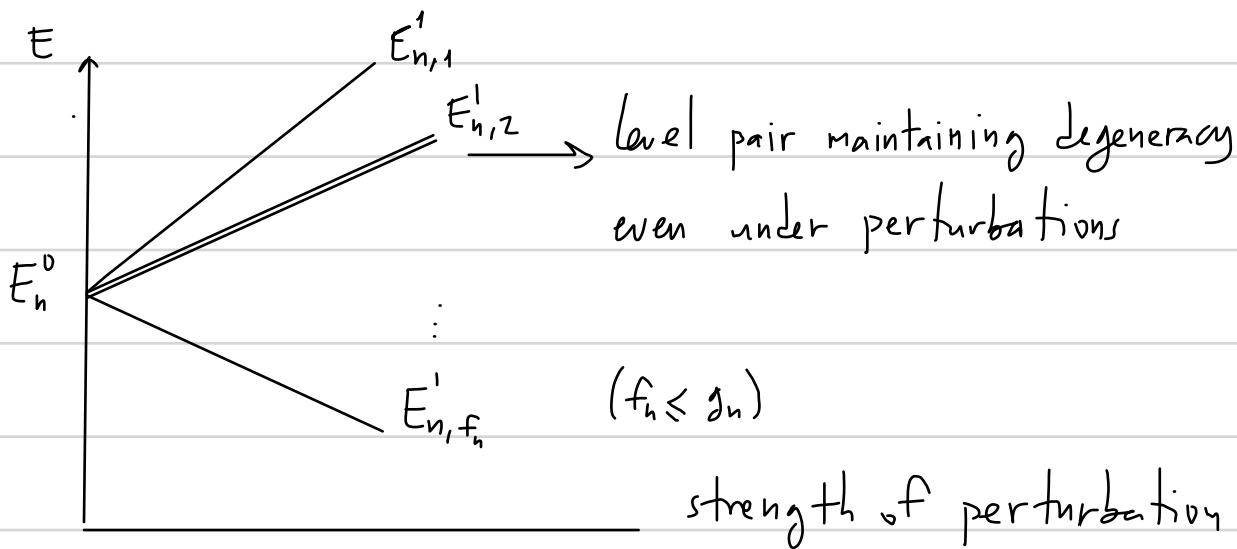
Degenerate pert. theory

Suppose energy E_n^0 is g_n -fold degenerate

↑
attention! my
notation differs from Cohen's

Def: $E_n^1 \equiv$ eigenspace of H_0 corresponding to E_n^0 , generated by eigenstates $|e_{n,i}^0\rangle, i=1, \dots, g_n$

In this case, the perturbation H^1 will tend to 'lift' or 'break' this degeneracy, either partially or totally.



Of course, any linear combination $|q\rangle = \sum_{j=1}^{g_n} c_j |e_{n,j}^0\rangle$ is also an eigenstate of H_0 with energy E_n^0 .

However (crucial point to understand): only certain, 'good' combinations will allow us to calculate the 1st order energy corrections $E_{n,i}^1$. These 'good' 0th-order states will be the correct basis for all further orders in the perturbation expansion.

Let us first see how this works in 1st order in energy.

- 0th- and 1st-order equations for the energy are still valid as before:

$$H_0 |\Psi_n^0\rangle = E_n^0 |\Psi_n^0\rangle \quad (0)$$

$$(H_0 - E_n^0) |\Psi_n^1\rangle + (H^1 - E_n^1) |\Psi_n^0\rangle = 0 \quad (1)$$

- However, due to the degeneracy in E_n^0 , it is not clear "a priori" which state " $|\Psi_n^0\rangle$ " should appear in eq. (1). (All we know is that it is some linear combination of a basis $\{|\psi_{n,i}^0\rangle\}$, as above).

- To find out which combinations are 'good' (i.e., solve eq. (1)), we multiply this eq. from the left using the basis vectors $\langle e_{n,i}^0 |$

$$\underbrace{\langle e_{n,i}^0 | (H_0 - E_n^0) | \Psi_n^1 \rangle}_{= 0, \text{ since } \langle e_{n,i}^0 | H_0 = \langle e_{n,i}^0 | E_n^0} + \langle e_{n,i}^0 | (H^1 - E_n^1) | \Psi_n^0 \rangle = 0$$

$$\rightarrow \boxed{\langle e_{n,i}^0 | H^1 | \Psi_n^0 \rangle = E_n^1 \langle e_{n,i}^0 | \Psi_n^0 \rangle}$$

Using $\sum_P \sum_{k=1}^{2r} |e_{P,k}^0 \times e_{P,k}^0| = \prod$:

$$\sum_{P,k} \langle e_{n,i}^0 | H^1 | e_{P,k}^0 \rangle \langle e_{P,k}^0 | \Psi_n^0 \rangle = E_n^1 \langle e_{n,i}^0 | \Psi_n^0 \rangle$$

Since $|\Psi_n^0\rangle$ is a combination only of $|e_{n,i}^0\rangle$ (i.e., basis states with $p=n$) then

$$\sum_{k=1}^{2n} \langle e_{n,i}^0 | H^1 | e_{n,k}^0 \rangle \langle e_{n,k}^0 | \Psi_n^0 \rangle = E_n^1 \langle e_{n,i}^0 | \Psi_n^0 \rangle$$

Simplifying the notation: $|\Psi_n^0\rangle \equiv |\psi^0\rangle$; $|\epsilon_{n,i}^0\rangle \equiv |i\rangle$

$$\sum_{k=1}^{g_n} \langle i | H' | k \rangle \langle k | \psi^0 \rangle = E_n^1 \langle i | \psi^0 \rangle \quad |i\rangle = 1, \dots, g_n \quad (*)$$

Def $H_n^1 = \text{restriction of } H' \text{ to the } E_n^0 \text{ subspace}$
 [i.e. the $g_n \times g_n$ "block" within H' that maps E_n^0 to E_n^0]

Within E_n^0 , $\sum |k\rangle\langle k| = 1$ → The eqs above are equivalent simply to

$$H_n^1 |\Psi^0\rangle = E_n^1 |\Psi^0\rangle$$

In other words: to find the 1st order energies $E_{n,k}^1$, we need to solve the eigenvalue equation for H_n^1 ! This equation will have solutions $E_{n,i}^1$, $i = 1 \dots f_n \leq g_n$ with corresponding orthonormal eigenvectors $|\Psi_{n,k}^0\rangle$. These vectors satisfy

$$E_{n,i}^1 = \langle \Psi_{n,i}^0 | H_n^1 | \Psi_{n,i}^0 \rangle$$

We can see that, for these 'good' 0th-order vectors $\{|\Psi_{n,i}^0\rangle\}$, the 1st order perturbation behaves just like in the nondegenerate case!

Note that may also still be partially degenerate ($f_n < g_n$). In this case, the 1st order perturbation will only partially 'lift' the original degeneracy in E_n^0 . The remaining degeneracy may or may not be lifted by higher-order corrections [for example, if the exact Hamiltonian $H_0 + H'$ is degenerate, then this will also be true in all orders of perturbation]

The 'good basis' theorem

If the degeneracy g_n (size of \mathcal{E}_n^0) is large, it may seem hopeless to obtain the 1st order corrections by the method above - because it requires diagonalizing a $g_n \times g_n$ matrix!

However, in many practical cases this can be done automatically, thanks to the following result:

Theorem: suppose we can find some hermitian operator A satisfying

- $[A, H_0] = 0$ [remember: this means we can choose a common basis of eigenvectors for both operators; in particular we can assume that the basis states $\{|i\rangle\} \in \mathcal{E}_n^0$ in eq. (*) above are also eigenvectors of A , ie $A|a_i\rangle = \alpha_i |a_i\rangle$]
- $\alpha_j \neq \alpha_k$ for $j \neq k$ (ie, A is nondegenerate within \mathcal{E}_n^0)
- $[A, H'] = 0$ too

In this case: $\{|a_i\rangle\}$ are in fact also the eigenstates of H'_n , with eigenvalues

$$E'_{n,i} = \langle a_i | H'_n | a_i \rangle$$

proof · since $[A, H'] = 0$, then

$$\begin{aligned}
 0 &= \langle a_j | [A, H'] | a_k \rangle = \underbrace{\langle a_j | A H' | a_k \rangle}_{= \alpha_j \langle a_j |} - \underbrace{\langle a_j | H' A | a_k \rangle}_{\alpha_k \langle a_k |} = (\alpha_j - \alpha_k) \langle a_j | H' | a_k \rangle \\
 &\quad \text{since } A \text{ Hermitian} \\
 &= (\alpha_j - \alpha_k) \langle a_j | H'_n | a_k \rangle \\
 &\quad (\text{since } |a_j\rangle, |a_k\rangle \in E_n^\otimes)
 \end{aligned}$$

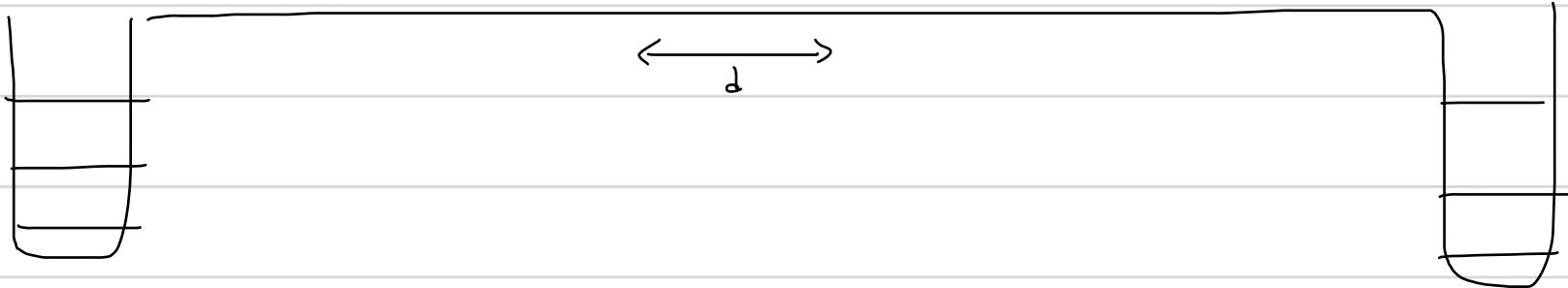
if $j \neq k \Rightarrow \alpha_j \neq \alpha_k$, so $\langle a_j | H'_n | a_k \rangle = 0$

$\rightarrow H'_n$ is diagonal in the $\{|a_j\rangle\}$ basis!

Note : We can easily extend the theorem above to situations where more than one 'label' is necessary to identify $\{|a_i\rangle\}$, i.e., where instead of a single observable A we have a set $A_1 \dots A_m$ that forms a C.S.C.O. within E_n^\otimes . If all these operators commute with H_0 and H' , the derivation above remains valid (the 'good' basis is then the common basis of the C.S.C.O.)

Example : consider again a particle in a symmetric ^{1D} double well, only now we consider all the levels of each well (not just the ground state)

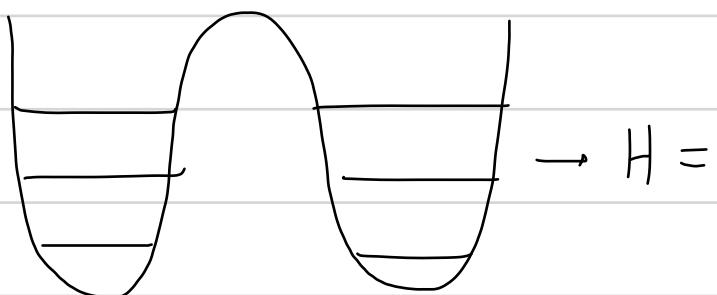
Consider 1st the limit where the wells are 'very far away' ($d \rightarrow \infty$)



In this case, there is no possibility of the particle tunneling from one well to the other. The eigenstates of this system are then just the states localized in each well ($|L_1\rangle, |L_2\rangle, |L_3\rangle \dots$ for the left well, and $|R_1\rangle, |R_2\rangle, |R_3\rangle \dots$ for the right well), with corresponding energies $E_1, E_2, E_3 \dots$. Each energy is doubly degenerate. We shall take this limit as "the"

$$H_0 = \begin{bmatrix} E_1 & & & \\ & E_1 & & \\ & & E_2 & \\ & & & E_2 \\ & & & & E_3 \\ & & & & & E_3 \\ & & & & & \ddots \end{bmatrix}$$

when the wells are not too far from each other, however, the particle will now have amplitudes to tunnel from one well to another



$$\rightarrow H =$$

$$\begin{bmatrix} \langle L_1 | & E_1 & A_{11} & 0 & A_{12} & 0 & A_{13} \\ \langle R_1 | & A_{11} & E_1 & A_{12} & 0 & A_{13} & 0 \\ \langle L_2 | & 0 & A_{12} & E_2 & A_{22} & 0 & A_{23} \\ \langle R_2 | & A_{12} & 0 & A_{22} & E_2 & A_{23} & 0 \\ \langle L_3 | & 0 & A_{13} & 0 & A_{23} & E_3 & A_{33} \\ \langle R_3 | & A_{13} & 0 & A_{23} & 0 & A_{33} & E_3 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}$$

(we assume the tunneling amplitudes A_{ij} are real for simplicity)

let us calculate the effect of this 'tunneling perturbation'
to 1st order in energy and 0th order in the eigenstates

$$|L_1\rangle|R_1\rangle|L_2\rangle|R_2\rangle|L_3\rangle|R_3\rangle \dots$$

$$H^1 = \langle L_1 | \begin{matrix} 0 & A_{11} & 0 & A_{12} & 0 & A_{13} \\ A_{11} & 0 & A_{12} & 0 & A_{13} & 0 \\ 0 & A_{12} & 0 & A_{22} & 0 & A_{23} \\ A_{12} & 0 & A_{22} & 0 & A_{23} & 0 \\ 0 & A_{13} & 0 & A_{23} & 0 & A_{33} \\ A_{13} & 0 & A_{23} & 0 & A_{33} & 0 \end{matrix} | R_1 \rangle$$

1st of all, let us look at the restrictions of H^1 to each degenerate subspace E_n^0 , spanned by $\{|L_n\rangle, |R_n\rangle\}$: they are all of the form $H_n^1 = \begin{bmatrix} 0 & A_{nn} \\ A_{nn} & 0 \end{bmatrix}$

Although it is simple to diagonalize these matrices directly, let us use the 'good basis' theorem. The 1st step is to identify a quantity which commutes with A , which is to say a symmetry of this Hamiltonian. This is easy to see if we note that this double well is invariant under the operation that swaps $|L\rangle$ and $|R\rangle$ (a reflection along the midpoint between the wells)

This corresponds to a parity observable A , that has 2 eigenvalues: +1 for states that are symmetric under $|L\rangle \leftrightarrow |R\rangle$, and -1 for states that

are antisymmetric under $|L\rangle \leftrightarrow |R\rangle$. Within each 2×2 subspace E_n^0 , spanned by $\{|L_n\rangle, |R_n\rangle\}$, the only states of these kinds are

$$|S_n\rangle = \frac{1}{\sqrt{2}} [|L_n\rangle + |R_n\rangle] \quad (\text{symmetric})$$

$$|A_n\rangle = \frac{1}{\sqrt{2}} [|L_n\rangle - |R_n\rangle] \quad (\text{antisymmetric})$$

It is easy to see that these are, in fact, the eigenstates of H_n^1 , with eigenvalues $\pm A_{nn}$

It follows that, to 1st order, the energies of the double well are

$$E_n \pm A_{nn} \equiv E_{\frac{S}{A}}$$

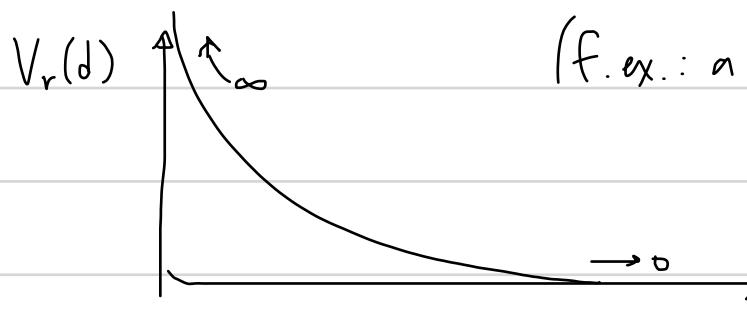
and the states $\{|S_n\rangle, |A_n\rangle\}$ form the 'good' basis

Notice the antisymmetric states have the lower energy, and that this energy becomes lower as A_{nn} increases. Meanwhile, the symmetric states have an energy that becomes higher as A_{nn} increases

Physical interpretation: "bonding" and "antibonding" states and chemical bonds

With some small extensions, we can use the double-well potential as a simple model for a chemical bond:

- let us suppose that the tunneling amplitudes A_{nn} depends on the distance d between the wells, more specifically that $A_{nn}(d)$ increases as d decreases (which makes physical sense: the wider the 'barrier' between the wells, the harder it should be for the electron to tunnel).
- Furthermore, suppose also that the wells themselves represent positive nuclei that repel each other, with a classical potential energy $V_r(d)$ of the form

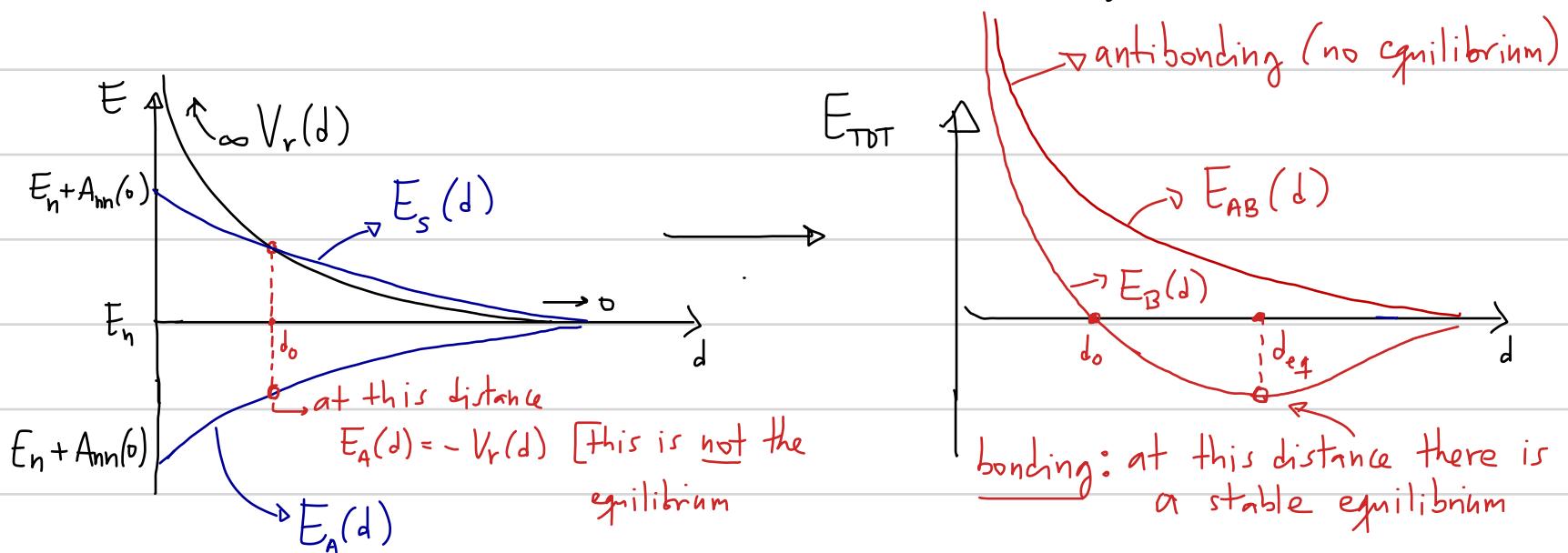


(f.ex.: a Coulomb energy $V_r(d) = \frac{+e^2}{4\pi\epsilon_0 \cdot d}$)

Then we can view the double well system as a 3-particle system (2 nuclei and a electron), with a total energy that depends on d and also on whether the electron is in an antibonding (symmetric) state or a bonding (antisymmetric) state

$$E_{TOT}(d) = V_r(d) + E_n \pm A_{nn}(d) \equiv E_{AB}^{\downarrow}(d)$$

- In the 1st case, the total energy decreases with d . This corresponds to a total force that repels the wells at any distance. No bond can be formed.
- In the 2nd case, however, the electron energy corresponds to an attractive force that counteracts the direct repulsion between the wells.
It may happen then that some distance d_{eq} exists where these forces cancel and a stable equilibrium thus can be found. (In terms of potential energy, d_{eq} corresponds to the value of d that minimizes the total energy $E_{TOT}(d)$)
This is the internatomic distance of the chemical bond!



Of course, to model real chemical bonds, we must consider more realistic 3D potential wells, and also the effect of other electrons etc. However, the basic qualitative features of this simple model remain valid.

Example (Griffiths 6.2)

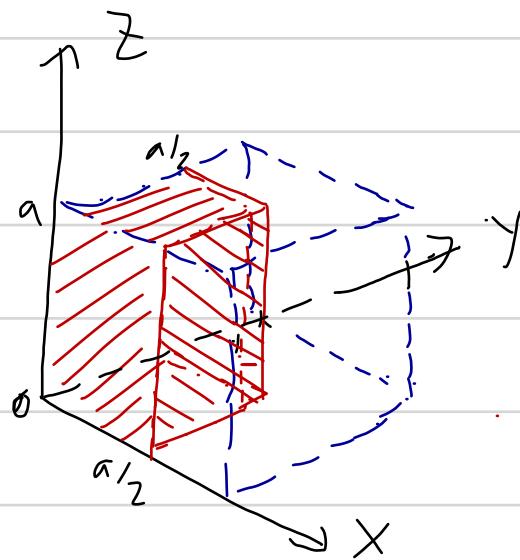
$$H_0 = \text{3D infinite cubical well} : \begin{cases} 0 & \text{if } 0 \leq x, y, z \leq a \\ \infty & \text{otherwise} \end{cases}$$

eigenstates $|n_x, n_y, n_z\rangle$, eigenenergies $(n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2 \pi^2}{2ma^2} ; n_j \geq 1$

ground state : $|111\rangle$, energy $E_0^0 = 3E$

1st excited state (3x deg.) : $E_1^0 = 6E$ ($\leftrightarrow |112\rangle, |121\rangle, |211\rangle$)

$$H' = \begin{cases} V', & 0 < x, y < a/2 \\ 0, & \text{otherwise} \end{cases} \quad [\text{acts only on } 1/4 \text{ of the full cube}]$$



perturbation to ground level : can use nondegenerate theory :

$$E_0^1 = \langle 111 | H' | 111 \rangle = \left(\frac{2}{a}\right)^3 \cdot V_0 \int_0^{a/2} dx \sin^2\left(\frac{\pi x}{a}\right) \cdot \int_0^{a/2} dy \sin^2\left(\frac{\pi y}{a}\right) \int_0^a dz \sin^2\left(\frac{\pi z}{a}\right) = V_0 / 4$$

perturbation to the 1st excited state : must use degenerate theory :

Solving using the 'good basis' theorem: use common symmetries of H_0 and H' :

1) both H_0 and H' are invariant under the exchange of $x \rightleftharpoons{} y$ axes
 $(\equiv$ reflection through the vertical plane $x=y$)

\rightarrow 'good' order of states must be combinations of $|112\rangle, |121\rangle, |211\rangle$ with definite parity $\Pi_{x \rightleftharpoons{} y}$. (ie, states $|4\rangle$ s.t. $|4\rangle \rightarrow \pm |4\rangle$ under the exchange of $x \rightleftharpoons{} y$ axes)

checking: under this operation

$$|112\rangle \rightarrow |112\rangle \quad (\text{an even state}) \quad \checkmark$$

$$|121\rangle \rightleftharpoons{} |211\rangle \quad (\text{these states do not have well-defined parity } \Pi_{x \rightleftharpoons{} y})$$

construct states with definite parity $\Pi_{x \rightleftharpoons{} y} : \frac{1}{\sqrt{2}}[|121\rangle \pm |211\rangle]$ [resp. even/odd]

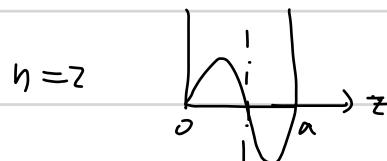
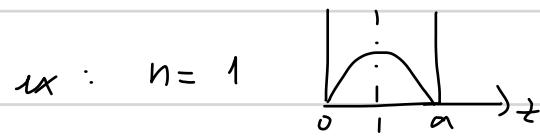
thus we obtain 1 state that is odd and 2 that are even under $x \rightleftharpoons{} y$

Since the odd state is uniquely determined, the theorem ensures that it must automatically be an element of the 'good basis'!

However, since this symmetry does not distinguish the 2 even states, we cannot (yet) say anything about which combinations of them are also elements of the 'good basis'. For this we need a second symmetry:

2) both H_0 and H^1 are unchanged under $z \xrightarrow{=} \frac{a}{2} - z$ (or $z \rightleftharpoons a-z$)
 [\equiv reflection through the horizontal plane $z = a/2$]

under this reflection, all eigenfunctions with $n_z = 1, 3, 5, \dots$ are even, and
 all eigenfunctions with $n_z = 2, 4, 6, \dots$ are odd (they have definite parity $\Pi_{z \rightleftharpoons a-z}$)



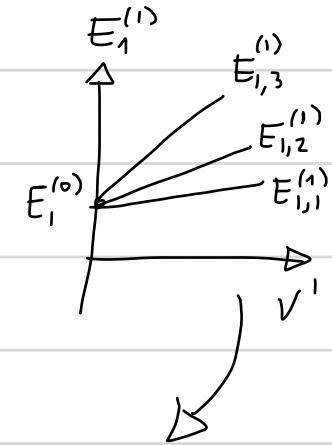
$\Rightarrow \frac{1}{\sqrt{2}}(|1z1\rangle \pm |211\rangle)$ are even; $|11z\rangle$ is odd

\Rightarrow The 3 states $\{|11z\rangle, \frac{1}{\sqrt{2}}(|1z1\rangle \pm |211\rangle)\}$ form a basis that can be completely classified according to common symmetries of H_0 and H^1

	$\Pi_{x \rightleftharpoons y}$	$\Pi_{z \rightleftharpoons a-z}$
$ 11z\rangle$	even	odd
$\frac{1}{\sqrt{2}}(1z1\rangle + 211\rangle)$	even	even
$\frac{1}{\sqrt{2}}(1z1\rangle - 211\rangle)$	odd	even

by the theorem, these states must form the 'good basis' of eigenstates of order 0.

$$\left\{ \begin{array}{l} |\Psi_{1,1}^{(0)}\rangle = \frac{1}{\sqrt{2}}(|1z1\rangle - |211\rangle); \quad E_{1,1}^{(0)} = \langle \Psi_{1,1}^{(0)} | H^1 | \Psi_{1,1}^{(0)} \rangle = \left(1 - \left(\frac{8}{3\pi}\right)^2\right) \frac{V}{4} \approx 0.72 \\ |\Psi_{1,2}^{(0)}\rangle = |11z\rangle; \quad E_{1,2}^{(0)} = \langle \Psi_{1,2}^{(0)} | H^1 | \Psi_{1,2}^{(0)} \rangle = \frac{V}{4} \\ |\Psi_{1,3}^{(0)}\rangle = \frac{1}{\sqrt{2}}(|1z1\rangle + |211\rangle); \quad E_{1,3}^{(0)} = \langle \Psi_{1,3}^{(0)} | H^1 | \Psi_{1,3}^{(0)} \rangle = \left(1 + \left(\frac{8}{3\pi}\right)^2\right) \frac{V}{4} \end{array} \right.$$



the perturbation completely splits this level

EXTRA : Further terms in degenerate PT

Neither CT nor Griffiths seem to discuss explicitly how to calculate the higher-order corrections. In many (but not all...) cases, this is straightforward:

For example: to obtain the 1st order correction $|\Psi_{n,i}^1\rangle$ to the 'good' 0th-order eigenstates $|\Psi_{n,i}^0\rangle$, we plug them, and the value of $E_{n,i}^1$, into the 1st-order eq

$$H_0 |\Psi_{n,i}^1\rangle + H^1 |\Psi_{n,i}^0\rangle = E_n^0 |\Psi_{n,i}^1\rangle + E_{n,i}^1 |\Psi_{n,i}^0\rangle$$

We now proceed as before, expanding $|\Psi_{n,i}^1\rangle$ in the complete basis of all 0th-order 'good' states

$$|\Psi_{n,i}^1\rangle = \sum_{m \neq n} \sum_{j_m=1}^{g_m} c_{m,j_m}^{(n,i)} |\Psi_{m,j_m}^0\rangle$$

(Again, terms with $m \neq n$ cancel out and can be excluded from the expansion)

Following the same steps as previously, we arrive at

$$|\Psi_{n,i}^1\rangle = \sum_{m \neq n} \sum_{j_m=1}^{g_m} \frac{\langle \Psi_{m,j_m}^0 | H^1 | \Psi_{n,i}^0 \rangle}{E_n^0 - E_m^0} |\Psi_{m,j_m}^0\rangle$$

In other words, we obtain an expression identical to the one in the nondegenerate case. The only difference is that we must use the 'good' 0th-order states in the expansions.

For the 2nd order energies, something similar usually happens—but not always. To understand why, let us take the 2nd-order equation

$$H_0 |\Psi_{n,i}^2\rangle + H^1 |\Psi_{n,i}^1\rangle = E_n^0 |\Psi_{n,i}^2\rangle + E_{n,i}^1 |\Psi_{n,i}^1\rangle + E_n^2 |\Psi_{n,i}^0\rangle$$

We now have 2 cases to consider

CASE I. $E_{n,i}^1$ is nondegenerate [i.e., the perturbation is 'lifted' in 1st order]

If $E_{n,i}^1$ is a nondegenerate value (in 1st order), then we can proceed just like in the 0th-order nondegenerate case. In this case $|\Psi_{n,i}^1\rangle$ is uniquely defined, so if we take the product with $\langle \Psi_{n,i}^0 |$ from the left we have as before

$$E_n^0 \cancel{\langle \Psi_{n,i}^0 |} \Psi_{n,i}^2 \rangle + \langle \Psi_{n,i}^0 | H^1 | \Psi_{n,i}^1 \rangle = E_n^0 \cancel{\langle \Psi_{n,i}^0 |} \Psi_{n,i}^2 \rangle + E_{n,i}^1 \cancel{\langle \Psi_{n,i}^0 |} \Psi_{n,i}^1 \rangle + E_n^2$$

since $|\Psi_{n,i}^1\rangle$ only contains $m \neq n$

$$E_{n,i}^2 = \langle \Psi_{n,i}^0 | H^1 \left(\sum_{m \neq n} \sum_{j_m=1}^{j_m} \frac{\langle \Psi_{m,j_m}^0 | H^1 | \Psi_{n,i}^0 \rangle}{E_n^0 - E_m^0} \right) | \Psi_{m,j_m}^0 \rangle$$

$$E_{n,i}^2 = \sum_{m \neq n} \sum_{j_m=1}^{j_m} \frac{|\langle \Psi_{m,j_m}^0 | H^1 | \Psi_{n,i}^0 \rangle|^2}{E_n^0 - E_m^0}$$

Thus, we again get an expression that is identical to the nondegenerate case.

CASE II: energy $E_{n,i}^1$ still degenerate in 1st order

However, if $E_{n,i}^1$ is still degenerate in 1st order, we have to again be more careful.

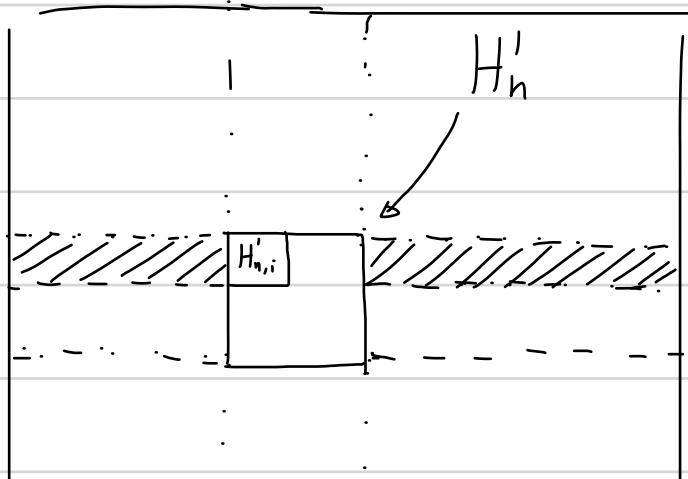
In this case there are several "good" states $\{|\Psi_{n,i,j}^0\rangle\}_{j=1}^{g_{ni}}$ with this same energy, which span a g_{ni} -dim subspace $E_{n,i}^0 \subset E_n^0$. Once again, it is not "a priori" clear which combinations of these states are the correct ('better') ones.

As before then, we choose a basis $\{|\Psi_{n,i,j}^0\rangle\}_{j=1}^{g_{ni}} \equiv \{|j\rangle\}$ for $E_{n,i}^0$ and multiply eq (2) from the left with $\langle j|$:

$$\begin{aligned}
 &= E_n^0 \langle j | \\
 &\cancel{\langle j | H_0 |\Psi_{n,i}^2\rangle + \langle j | H^\dagger |\Psi_{n,i}^1\rangle} = E_n^0 \cancel{\langle j | \Psi_{n,i}^2\rangle} + \underbrace{E_{n,i}^1 \cancel{\langle j | \Psi_{n,i}^1\rangle}}_{=0 \text{ since } |\Psi_{n,i}^1\rangle \text{ only contains } m \neq n} + E_{n,i}^2 \langle j | \Psi_{n,i}^0\rangle \\
 &\rightarrow \boxed{\langle j | H^\dagger |\Psi_{n,i}^1\rangle = E_{n,i}^2 \langle j | \Psi_{n,i}^0\rangle} \quad j=1, \dots, g_{ni} \quad (\times \times)
 \end{aligned}$$

This is similar, but not quite the same, as the eigenvalue equation we solved to find $E_{n,i}^1$. Note that here we have two different kets on each side ($|\Psi_{n,i}^1\rangle$ on the left, and $|\Psi_{n,i}^0\rangle$ on the right)

Note also that, while $|\Psi_{n,i}^0\rangle$ and $|j\rangle$ are both $\in E_n^0$, the state $|\Psi_{n,i}^1\rangle$ only contains $|\Psi_{m,n}^0\rangle$ with $m \neq n$. In other words, the term $\langle j | H^\dagger |\Psi_{n,i}^1\rangle$ only contains elements from off-diagonal blocks of H^\dagger that connects $E_{n,i}^0$ to the other E_m^0 ($m \neq n$) [Eq]



$\langle j | H' | \Psi_{n,i}^1 \rangle$ contains only matrix elements of H' belonging to the hatched area in the figure, not including the diagonal 'block' H'_n

(remember: we used the elements of H'_n to calculate the 1st order corrections)

It may be a bit harder to see, but the system (***) is also an eigenvalue equation. To understand this, rewrite the expression for $|\Psi_{n,i}^1\rangle$ above:

$$|\Psi_{n,i}^1\rangle = \left(\sum_{m \neq n} \sum_{j_m=1}^{g_m} \frac{|\Psi_{m,j_m}^0\rangle \langle \Psi_{m,j_m}^0|}{E_n^0 - E_m^0} \right) H' |\Psi_{n,i}^0\rangle$$

replacing this in (**)

$$\langle j | \left(H' \sum_{m \neq n} \sum_{j_m=1}^{g_m} \frac{|\Psi_{m,j_m}^0\rangle \langle \Psi_{m,j_m}^0| H'}{E_n^0 - E_m^0} \right) |\Psi_{n,i}^0\rangle = E_{n,i}^2 \langle j | \Psi_{n,i}^0 \rangle \quad j=1, \dots, g_{n,i}$$

We can now recognize this as the eigenvalue equation for the operator

$$\left(H' \sum_{m \neq n} \sum_{j_m=1}^{g_m} \frac{|\Psi_{m,j_m}^0\rangle \langle \Psi_{m,j_m}^0| H'}{E_n^0 - E_m^0} \right)_{n_i}$$

(The index n_i means that we are looking only at the restriction of the operator in parentheses to the $g_{n,i} \times g_{n,i}$ "block" corresponding to the subspace $E_{n,i}^0$). The eigenvalues $E_{n,i,k}^2$; $k=1 \dots g_{n,i}$ will give the 2nd order corrections, and the corresponding eigenstates are the "better" combinations