

# ADVANCED QUANTUM PHYSICS

## Handout 2

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- ▶ Time-independent Perturbation Theory
- ▶ The variational method

# Approximate Methods

- Very few problems in Quantum Mechanics can be solved exactly
  - we often need to resort to approximations of various type
- In this section of the course, we will look at :
  - time-independent perturbation theory
  - the variational method (including Rayleigh-Ritz)
- Later in the course, we will consider :
  - time-dependent perturbation theory
  - approximations used in atomic/molecular structure
    - ( central-field, Hartree-Fock, Born-Oppenheimer, ... )

# Perturbation Theory

- In many circumstances, e.g. incorporating relativistic effects,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}_{\text{rel}}$$

or placing a given system in an external electric or magnetic field,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}_{E,B}$$

an effect of interest will only slightly modify a known Hamiltonian,  $H^{(0)}$

- In *perturbation theory*, corrections to the eigenstates of the leading-order (“zeroth-order”) unperturbed Hamiltonian  $H^{(0)}$  are obtained as a series of successively smaller terms: first-order, second-order, ...
- Here, we introduce perturbation theory by considering time-independent perturbations within the framework of “ordinary” quantum mechanics

In its ultimate, time-dependent, relativistically covariant, field-theoretic form, perturbation theory is the central calculational technique in particle physics, for example (Feynman diagrams)

# Time-Independent Perturbation Theory

- Consider a Hamiltonian  $H$  of the form

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

where  $\hat{H}^{(0)}$  is an unperturbed “zeroth-order” Hamiltonian with eigenstates  $|n^{(0)}\rangle$ , and eigenvalues  $E_n^{(0)}$ , which are assumed to be already known,

$$\hat{H}^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle ; \quad \langle n^{(0)}|m^{(0)}\rangle = \delta_{nm}$$

and where  $\hat{H}'$  is a “small” time-independent perturbation such that

$$\langle n^{(0)}|\hat{H}'|n^{(0)}\rangle \ll E_n^{(0)}$$

- In perturbation theory, the (unknown) eigenfunctions and eigenvalues of  $H$ ,

$$(\hat{H}^{(0)} + \hat{H}')|n\rangle = E_n|n\rangle$$

are obtained by a successive series of corrections, each of order  $\langle H' \rangle / \langle H^{(0)} \rangle$  with respect to the one before

## Time Independent Perturbation Theory (2)

- To keep track of terms which are of the same order in  $\langle H' \rangle / \langle H^{(0)} \rangle$ , we extract from  $H'$  a dimensionless real parameter  $\lambda$  which characterises the size of the perturbation :

$$\hat{H}' \equiv \lambda \hat{H}^{(1)}$$

(  $\lambda$  will not appear in any expressions for observable quantities )

The equation to be solved is then

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)}) |n\rangle = E_n |n\rangle \quad (2.5.1)$$

- In perturbation theory, we look for solutions of equation (2.5.1) which can be expressed as a power series in  $\lambda$ , with successively smaller terms :

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots = \sum_m \lambda^m E_n^{(m)} \quad (2.5.2)$$

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots = \sum_m \lambda^m |n^{(m)}\rangle$$

## Time Independent Perturbation Theory (3)

- This form of solution implicitly assumes that the eigenstates of the system evolve smoothly (“adiabatically”) away from the unperturbed states as the perturbation is gradually “switched on”
- Substituting equation (2.5.2) into equation (2.5.1) gives

$$\begin{aligned} & \left( \hat{H}^{(0)} + \lambda \hat{H}^{(1)} \right) \left[ |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \right] \\ &= \left[ E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right] \left[ |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots \right] \end{aligned} \tag{2.6.1}$$

- We begin by using equation (2.6.1) to obtain the first-order changes, of order  $\lambda$ , to the unperturbed energies and eigenstates for each  $n$  :

$$\Delta E_n^{(1)} = \lambda E_n^{(1)} ; \quad |\Delta n\rangle^{(1)} = \lambda |n^{(1)}\rangle$$

We then obtain the second-order changes to the energies :

$$\Delta E_n^{(2)} = \lambda^2 E_n^{(2)}$$

(the procedure can be extended to higher orders if necessary)

## First-order Perturbation Theory

- Equating terms of order  $\lambda$  on either side of equation (2.6.1) gives

$$\hat{H}^{(0)}|n^{(1)}\rangle + \hat{H}^{(1)}|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle \quad (2.7.1)$$

- To isolate  $E_n^{(1)}$ , take the inner product of equation (2.7.1) with  $\langle n^{(0)}|$  :

$$\langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle + \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle = E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle + E_n^{(1)}$$

Since  $\langle n^{(0)}|\hat{H}^{(0)} = E_n^{(0)}\langle n^{(0)}|$ , the first terms on either side above cancel, leaving

$$E_n^{(1)} = \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \quad (2.7.2)$$

- The first order energy correction  $\Delta E_n^{(1)} = \lambda E_n^{(1)}$  for the state  $|n^{(0)}\rangle$  is therefore

$$\boxed{\Delta E_n^{(1)} = \langle n^{(0)}|\hat{H}'|n^{(0)}\rangle} \quad (2.7.3)$$

The energy correction does not depend on the unphysical parameter  $\lambda$  ;  
→ the right-hand side above is (in principle) a known, calculable quantity

## First-order Perturbation Theory (2)

Next we obtain the first-order wavefunction correction  $|\Delta n\rangle^{(1)} = \lambda|n^{(1)}\rangle$  :

- Assume that the first-order term  $|n^{(1)}\rangle$  is expressible as a linear combination of the complete set of unperturbed eigenstates  $|n^{(0)}\rangle$  :

$$|n^{(1)}\rangle = \sum_m \langle m^{(0)} | n^{(1)} \rangle |m^{(0)}\rangle \quad (2.8.1)$$

To find  $|n^{(1)}\rangle$  for given  $n$ , we need to determine the overlap coefficients  $\langle m^{(0)} | n^{(1)} \rangle$  for all possible values of  $m$

- For  $m \neq n$ , these coefficients can (potentially) be found by taking the inner product of equation (2.7.1) with  $\langle m^{(0)} |$  :

$$\langle m^{(0)} | \hat{H}^{(0)} | n^{(1)} \rangle + \langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = E_n^{(0)} \langle m^{(0)} | n^{(1)} \rangle$$

Setting  $\langle m^{(0)} | \hat{H}^{(0)} = E_m^{(0)} \langle m^{(0)} |$  in the first term above then gives

$$E_m^{(0)} \langle m^{(0)} | n^{(1)} \rangle + \langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = E_n^{(0)} \langle m^{(0)} | n^{(1)} \rangle \quad (2.8.2)$$

## First-order Perturbation Theory (3)

- Provided the unperturbed states  $|m^{(0)}\rangle$  and  $|n^{(0)}\rangle$  have different energies (i.e. are *non-degenerate*), equation (2.8.2) rearranges to give

$$\langle m^{(0)} | n^{(1)} \rangle = \frac{\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \quad (E_m^{(0)} \neq E_n^{(0)}) \quad (2.9.1)$$

- However, if  $|m^{(0)}\rangle$  has the same energy as  $|n^{(0)}\rangle$  (i.e. if the states are *degenerate*), then equation (2.8.2) reduces just to the condition

$$\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = 0 \quad (m \neq n, \quad E_m^{(0)} = E_n^{(0)}) \quad (2.9.2)$$

and the overlap  $\langle m^{(0)} | n^{(1)} \rangle$  remains undetermined

- We will see below that, for initially degenerate states, it is always possible to arrange for condition (2.9.2) to be satisfied, thereby allowing a perturbation theory solution to be obtained

The value of the overlap  $\langle m^{(0)} | n^{(1)} \rangle$  for initially degenerate states can still not be determined, but this has no observable consequences

## First-order Perturbation Theory (4)

- The standard, most convenient, choice is to fix the form of the perturbed eigenstates by setting all indeterminate overlaps to zero :

$$\langle m^{(0)} | n^{(1)} \rangle \equiv 0 \quad (m \neq n, \quad E_m^{(0)} = E_n^{(0)}) \quad (2.10.1)$$

The overlap coefficient for the “trivial” case  $m = n$  also cannot be determined and is set to zero :

$$\langle n^{(0)} | n^{(1)} \rangle \equiv 0 \quad (2.10.2)$$

Note that we have already determined the (observable) first-order energy correction  $\Delta E_n^{(1)}$  without needing to know the value of any such overlaps

Note also that the wavefunction itself is not directly observable; some arbitrariness in its precise form is not *per se* a problem

- With all indeterminate overlaps chosen to be zero, the first-order wavefunction correction of equation (2.8.1) becomes

$$|n^{(1)}\rangle = \sum_{E_m^{(0)} \neq E_n^{(0)}} \langle m^{(0)} | n^{(1)} \rangle |m^{(0)}\rangle \quad (2.10.3)$$

## First-order Perturbation Theory (5)

- Substituting for  $\langle m^{(0)}|n^{(1)}\rangle$  from equation (2.9.1) then gives

$$|n^{(1)}\rangle = \sum_{E_m^{(0)} \neq E_n^{(0)}} \frac{\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle \quad (2.11.1)$$

- To first-order, the perturbed eigenstate  $|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle$  is then

$$|n\rangle = |n^{(0)}\rangle + \sum_{E_m^{(0)} \neq E_n^{(0)}} |m^{(0)}\rangle \frac{\langle m^{(0)}|\hat{H}'|n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}} \quad (2.11.2)$$

The “book-keeping” parameter  $\lambda$  again does not appear in the final result ; only calculable matrix elements of the given perturbation  $H'$  are involved

## Second-order Perturbation Theory

- Equating terms of order  $\lambda^2$  on each side of equation (2.6.1) gives

$$\hat{H}^{(0)}|n^{(2)}\rangle + \hat{H}^{(1)}|n^{(1)}\rangle = E_n^{(0)}|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle \quad (2.12.1)$$

- Taking the inner product with  $\langle n^{(0)}|$ , cancelling the first terms on each side, and setting the indeterminate overlap  $\langle n^{(0)}|n^{(1)}\rangle$  to zero, leaves

$$\langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle = E_n^{(2)}$$

- Substituting for  $|n^{(1)}\rangle$  from equation (2.10.3) in the left-hand side then gives

$$E_n^{(2)} = \sum_{E_m^{(0)} \neq E_n^{(0)}} \langle m^{(0)}|n^{(1)}\rangle \langle n^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle \quad (2.12.2)$$

- Substituting for  $\langle m^{(0)}|n^{(1)}\rangle$  from equation (2.9.1), this is

$$E_n^{(2)} = \sum_{E_m^{(0)} \neq E_n^{(0)}} \frac{|\langle m^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} \quad (2.12.3)$$

## Second-order perturbation theory (2)

- Hence the second-order correction  $\Delta E_n^{(2)} = \lambda^2 E_n^{(2)}$  to the energy of the state  $|n^{(0)}\rangle$  is given by

$$\Delta E_n^{(2)} = \sum_{E_m^{(0)} \neq E_n^{(0)}} \frac{|\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

(2.13.1)

The unphysical parameter  $\lambda$  again does not appear in the final result

*For completeness*, the appendix demonstrates explicitly that  $\Delta E_n^{(2)}$  does not depend on any indeterminate overlaps  $\langle m^{(0)} | n^{(1)} \rangle$

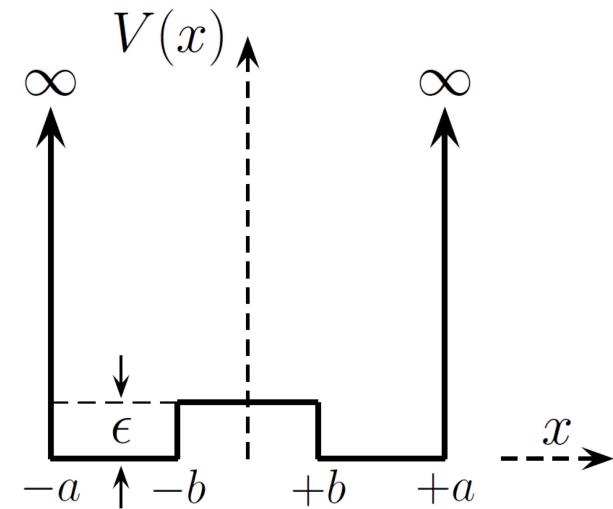
- It only remains to show that condition (2.9.2) can always be satisfied for any pair of initially degenerate states

First though we look at some examples involving only non-degenerate unperturbed energy levels ...

*(see slide 2.41 for a summary of the results obtained so far)*

## EXAMPLE : Infinite square well with central bump

$$\hat{H}' = \begin{cases} \epsilon & |x| < b \\ 0 & \text{otherwise} \end{cases}$$



The Schrödinger's eqn. can be solved, but only with a lot of work (numerical or graphical)

- For an infinite square well covering  $-a < x < a$ , the unperturbed energies and eigenfunctions (without the bump) are (see slide 1.37)

$$E_n^{(0)} = \frac{\hbar^2}{2m} \frac{n^2 \pi^2}{4a^2} = n^2 E_0$$

$$|n^{(0)}\rangle = \psi_n(x) = \sqrt{\frac{1}{a}} \sin \left[ \frac{n\pi}{2a} (x + a) \right]$$

$\left. \right\} (n = 1, 2, 3, \dots)$

where  $E_0$  is the unperturbed ground state energy :  $E_0 \equiv E_1^{(0)} = \frac{\hbar^2 \pi^2}{8ma^2}$   
 $(n = 1)$

## Example: central bump (2)

- The first-order correction to the unperturbed energy  $E_n^{(0)}$  is given by

$$\Delta E_n^{(1)} = \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle = \epsilon \int_{-b}^{+b} |\psi_n(x)|^2 dx$$

Substituting for the unperturbed wavefunction  $\psi_n(x)$  this is

$$\begin{aligned} \Delta E_n^{(1)} &= \frac{\epsilon}{a} \int_{-b}^{+b} \sin^2 \left[ \frac{n\pi}{2a}(x + a) \right] dx \\ &= \epsilon \left[ \frac{b}{a} - \frac{(-1)^n}{n\pi} \sin \left( \frac{n\pi b}{a} \right) \right] \end{aligned} \tag{2.15.1}$$

- In particular :

ground state ( $n = 1$ )

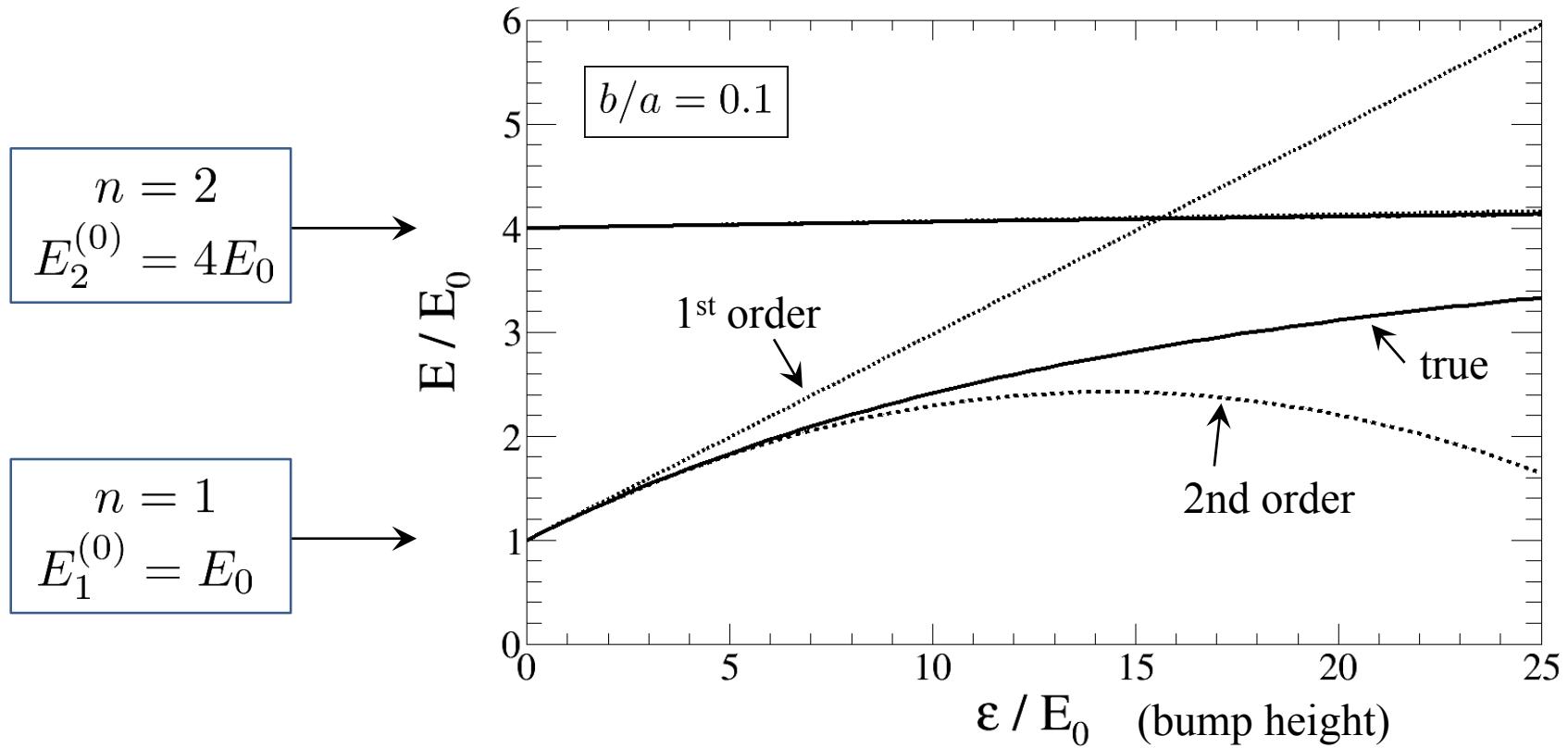
first excited state ( $n = 2$ )

$$\Delta E_1^{(1)} = \frac{\epsilon}{a} \left[ b + \frac{a}{\pi} \sin \left( \frac{\pi b}{a} \right) \right] ; \quad \Delta E_2^{(1)} = \frac{\epsilon}{a} \left[ b - \frac{a}{2\pi} \sin \left( \frac{2\pi b}{a} \right) \right]$$

- The first-order correction is tangential to the true solution at  $\epsilon = 0$  ...

### Example: central bump (3)

- e.g. the plot below shows the true and perturbation theory energies as a function of the height,  $\varepsilon$ , of the bump, for a bump of width  $b/a = 0.1$  :  
[ in units of the unperturbed ground state energy  $E_0 \equiv \hbar^2\pi^2/(8ma^2)$  ]



(For  $n = 2$  , the energy differences are too small to be visible)

## Example: central bump (4)

- For a narrow bump,  $b \ll a$ , equation (2.15.1) gives approximately

$$\Delta E_n^{(1)} \approx \frac{\epsilon b}{a} [1 - (-1)^n]$$

In particular :      ground state ( $n = 1$ )      first excited state ( $n = 2$ )

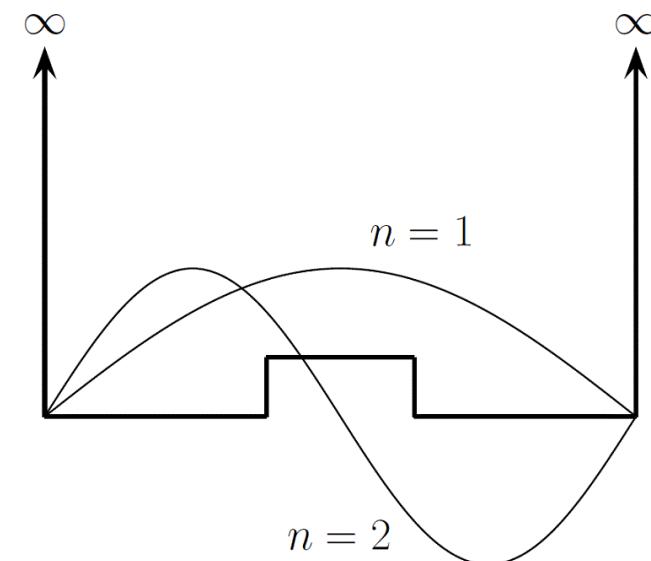
$$\Delta E_1^{(1)} \approx \frac{2\epsilon b}{a}; \quad \Delta E_2^{(1)} \approx 0$$

- The small energy correction for  $n = 2$  is qualitatively as expected from the form of the unperturbed wavefunctions :

At  $x = 0$  (where the bump is) :

- the  $n = 1$  wavefunction is *maximal*
- the  $n = 2$  wavefunction *vanishes*

Hence we expect the matrix element  $\langle n | H' | n \rangle$  to be much smaller for  $n = 2$  than for  $n = 1$



## Example: central bump (5)

- The *second-order* energy corrections are given by equation (2.13.1), as an infinite sum over terms involving matrix elements of the form

$$\begin{aligned}\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle &= \epsilon \int_{-b}^{+b} \psi_m^*(x) \psi_n(x) dx \\ &= \frac{\epsilon}{a} \int_{-b}^{+b} \sin\left(\frac{m\pi}{2a}(x+a)\right) \sin\left(\frac{n\pi}{2a}(x+a)\right) dx\end{aligned}$$

- If  $m$  and  $n$  are both even, or both odd, evaluating the integral gives

$$\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle = \frac{2\epsilon}{\pi} \left[ \frac{(-1)^{(m-n)/2}}{(m-n)} \sin\left(\frac{(m-n)\pi b}{2a}\right) - \frac{(-1)^{(m+n)/2}}{(m+n)} \sin\left(\frac{(m+n)\pi b}{2a}\right) \right]$$

If  $m$  is odd and  $n$  is even, or *vice versa*, the integral *vanishes* :

$$\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle = 0 \quad (m+n \text{ odd}) \tag{2.18.1}$$

- The second-order energies obtained from equation (2.13.1) for  $n = 1$  and  $n = 2$  are shown on slide 2.16, and move closer to the true solution

## Example: central bump (6)

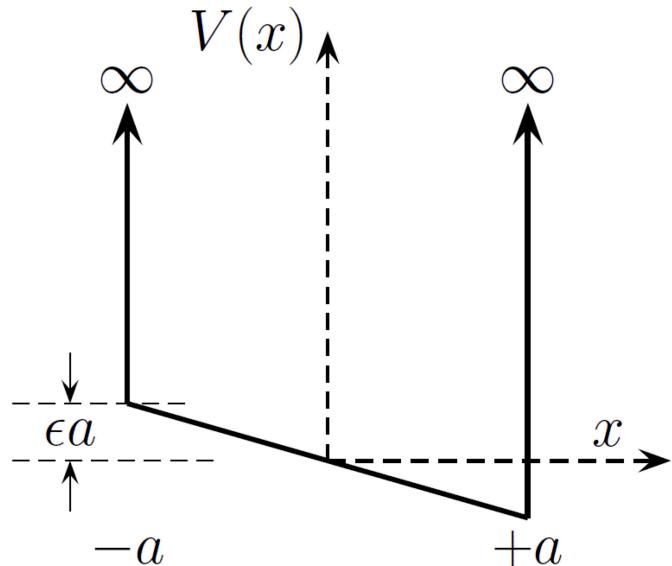
- Finally, the *first-order wavefunctions* are given by equation (2.11.2), involving an infinite sum over the same matrix elements as on slide 2.18
- Because of the matrix element property of equation (2.18.1), the symmetry of the wavefunctions is preserved :
  - states which are initially even (odd) remain even (odd) at first-order (consistent with the fact that the central-bump potential  $V(x)$  is symmetric)
- Each term in the infinite sum satisfies the boundary conditions at  $|x| = a$  and  $|x| = b$  (because each  $|m^{(0)}\rangle$  does) :
$$\psi(\pm a) = 0; \quad \psi, \psi' \text{ continuous at } x = \pm b$$
  - so do the first-order perturbed wavefunctions
- Overall conclusion :
  - perturbation theory gives sensible results for both the eigenstate energies and the corresponding wavefunctions

## EXAMPLE : Infinite square well in an electric field

- Applying an electric field  $\mathcal{E}$  corresponds to adding a perturbation  $\hat{H}' = -q\mathcal{E}x$

→ consider :  $\boxed{\hat{H}' = \epsilon x}$

In this case, no true solution of Schrödinger's equation is available for comparison



- The first-order energy corrections all *vanish* (by symmetry) :

$$\Delta E_n^{(1)} = \epsilon \int_{-a}^{+a} x |\psi_n(x)|^2 dx = \frac{\epsilon}{a} \int_{-a}^{+a} x \sin^2 \left( \frac{n\pi}{2a}(x+a) \right) dx = 0$$

(this is a 1D example of a *parity selection rule* – see later)

- At first order, only the wavefunctions change:

$$\Delta |n^{(1)}\rangle = \frac{\epsilon}{E_0} \sum_{m \neq n} |m^{(0)}\rangle \frac{\langle m^{(0)} | x | n^{(0)} \rangle}{n^2 - m^2}$$

$$\begin{cases} E_n^{(0)} = n^2 E_0 \\ E_m^{(0)} = m^2 E_0 \end{cases}$$

## Example: electric field (2)

- This requires evaluation of the matrix elements of the operator  $x$  between unperturbed states with  $m \neq n$ :

$$\begin{aligned}\langle m^{(0)} | x | n^{(0)} \rangle &= \int_{-a}^{+a} x \psi_m^*(x) \psi_n(x) dx \\ &= \frac{1}{a} \int_{-a}^{+a} x \sin\left(\frac{m\pi}{2a}(x+a)\right) \sin\left(\frac{n\pi}{2a}(x+a)\right) dx\end{aligned}$$

- If  $m, n$  are both even, or both odd, then the integral above vanishes (by symmetry); otherwise, we find

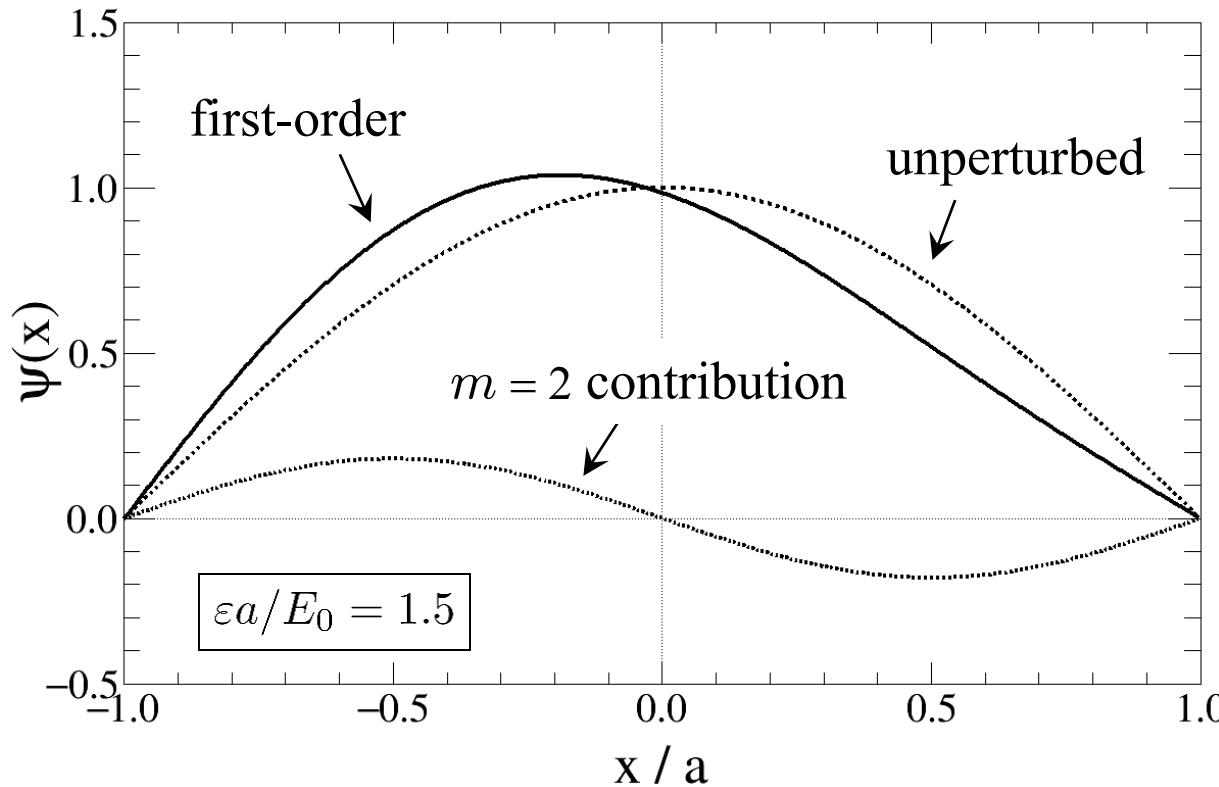
$$\langle m^{(0)} | x | n^{(0)} \rangle = -\frac{16a}{\pi^2} \frac{mn}{(m^2 - n^2)^2} \quad (m+n \text{ odd})$$

- Hence the change in the wavefunctions, to first-order, is

$$\Delta |n\rangle^{(1)} = \frac{\epsilon a}{E_0} \frac{16n}{\pi^2 \sqrt{a}} \sum_{m+n \text{ odd}} \frac{m}{(m^2 - n^2)^3} \sin\left(\frac{m\pi}{2a}(x+a)\right)$$

## Example: electric field (3)

- For the ground state ( $n = 1$ ), for example, only antisymmetric states (with even  $m$ ) contribute to the sum, and  $m = 2$  overwhelmingly dominates :



The  $m = 4, 6, 8, \dots$  contributions are too small to be visible

- The perturbed wavefunctions preserve the boundary conditions  $\psi(\pm a) = 0$ , but no longer have definite symmetry
  - [ as expected, because neither does the overall potential  $V(x)$  ]

## Example: electric field (4)

- The leading contribution to the energy corrections is *quadratic* (second-order) :

$$\Delta E_n^{(2)} = \frac{\epsilon^2}{E_0} \sum_{m \neq n} \frac{|\langle m^{(0)} | x | n^{(0)} \rangle|^2}{n^2 - m^2}$$

$$\Rightarrow \frac{\Delta E_n^{(2)}}{E_n^{(0)}} = - \left( \frac{\epsilon a}{E_0} \right)^2 \left( \frac{16}{\pi^2} \right)^2 \sum_{m+n \text{ odd}} \frac{m^2}{(m^2 - n^2)^3}$$

- For the ground state ( $n = 1$ ), again only even values of  $m$  contribute and the sum is overwhelmingly dominated by the  $m = 2$  contribution :

$$\begin{aligned} \frac{\Delta E_1^{(2)}}{E_1^{(0)}} &= - \left( \frac{\epsilon a}{E_0} \right)^2 \left( \frac{16}{\pi^2} \right)^2 \sum_{m=2,4,6,\dots} \frac{m^2}{(m^2 - 1)^3} \\ &= - \left( \frac{\epsilon a}{E_0} \right)^2 \left( \frac{16}{\pi^2} \right)^2 \left[ \frac{4}{27} + \frac{16}{15^3} + \frac{36}{35^3} + \dots \right] \\ |m\rangle &= |2\rangle \quad |4\rangle \quad |6\rangle \end{aligned}$$

## EXAMPLE : Harmonic oscillator + linear perturbation

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \epsilon\hat{x}$$

- The zeroth-order (harmonic oscillator) eigenstates,  $|n\rangle \equiv |n^{(0)}\rangle$ , are given on slide 1.38; the first-order energy corrections are :

$$\Delta E_n^{(1)} = \langle n | \hat{H}' | n \rangle = \epsilon \langle n | \hat{x} | n \rangle = \epsilon \int_{-\infty}^{+\infty} x |\psi_n(x)|^2 dx$$

- This is easiest evaluated using ladder operators (slide 1.41) :

$$\begin{aligned} \hat{x} &= \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger) & \left\{ \begin{array}{l} \hat{a}|n\rangle = \sqrt{n}|n-1\rangle \\ \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \end{array} \right. \\ \Rightarrow \quad \langle n | \hat{x} | n \rangle &\propto \langle n | \hat{a} | n \rangle + \langle n | \hat{a}^\dagger | n \rangle \\ &= \sqrt{n}\langle n | n-1 \rangle + \sqrt{n+1}\langle n | n+1 \rangle = 0 \end{aligned}$$

- Hence the first-order energy shift *vanishes* for all  $n$  :

$$\boxed{\Delta E_n^{(1)} = \langle n | \hat{H}' | n \rangle = 0} \quad (n = 0, 1, 2, \dots)$$

## Example: perturbed harmonic oscillator (2)

- The second-order energy correction,

$$\Delta E_n^{(2)} = \sum_{m \neq n} \frac{|\langle m | \hat{H}' | n \rangle|^2}{E_n^{(0)} - E_m^{(0)}} = \epsilon^2 \sum_{m \neq n} \frac{|\langle m | \hat{x} | n \rangle|^2}{E_n^{(0)} - E_m^{(0)}}$$

receives contributions only from neighbouring levels,  $m = n \pm 1$  :

$$\begin{aligned}\langle n-1 | \hat{a} | n \rangle &= \sqrt{n} \quad \Rightarrow \quad \langle n-1 | \hat{x} | n \rangle = \sqrt{\frac{\hbar}{2m\omega}} \sqrt{n} \\ \langle n+1 | \hat{a}^\dagger | n \rangle &= \sqrt{n+1} \quad \Rightarrow \quad \langle n+1 | \hat{x} | n \rangle = \sqrt{\frac{\hbar}{2m\omega}} \sqrt{n+1}\end{aligned}$$

All other terms vanish :  $\langle m | \hat{x} | n \rangle = 0$  for  $m \neq n \pm 1$

- Hence, to second-order, the perturbed energies are (for  $n = 0, 1, 2, \dots$ )

$$E_n = E_n^{(0)} + \frac{\hbar\epsilon^2}{2m\omega} \left( \frac{n}{E_n^{(0)} - E_{n-1}^{(0)}} + \frac{n+1}{E_n^{(0)} - E_{n+1}^{(0)}} \right)$$

## Example: perturbed harmonic oscillator (3)

- Substituting the unperturbed energies  $E_n^{(0)} = \left(n + \frac{1}{2}\right) \hbar\omega$  then gives the second-order energies as

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega - \frac{\epsilon^2}{2m\omega^2} \quad (2.26.1)$$

- This is, in fact, the *true* solution, as can be seen by writing the overall potential as

$$V(x) = \frac{1}{2}m\omega^2 \hat{x}^2 + \epsilon \hat{x} = \frac{1}{2}m\omega^2 \left(x + \frac{\epsilon}{m\omega^2}\right)^2 - \frac{\epsilon^2}{2m\omega^2}$$

This is a harmonic oscillator, still with frequency  $\omega$ , but with the central position shifted,

$$x \rightarrow x' = x + \epsilon/(m\omega^2),$$

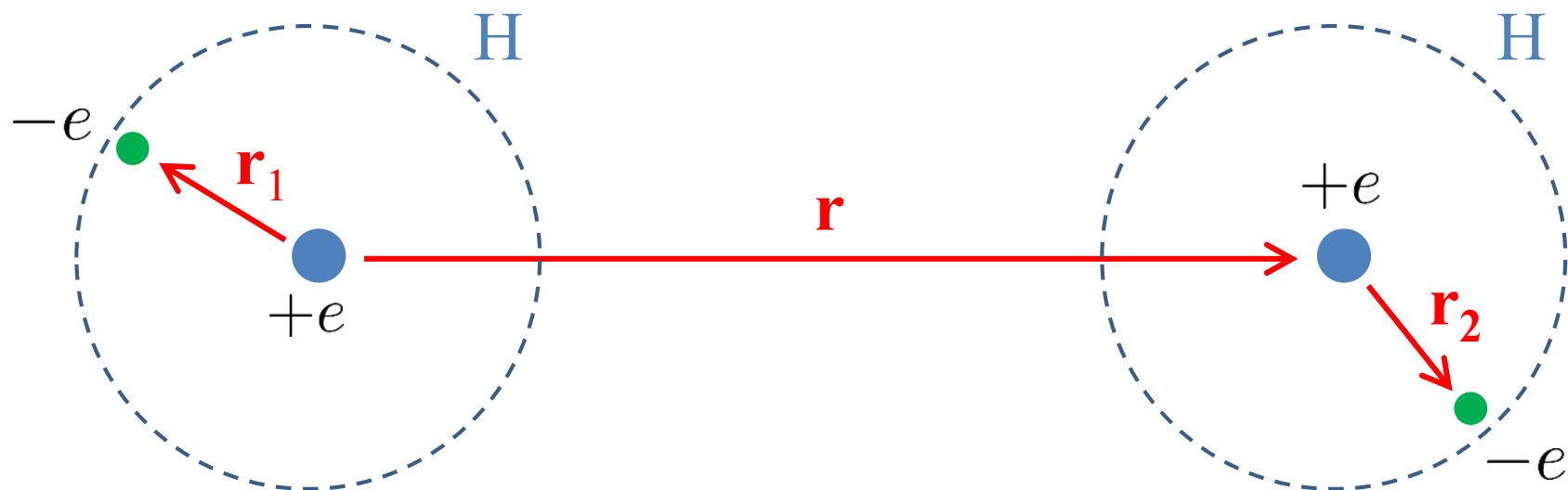
and with all energy levels lowered by a common amount :

$$E_n \rightarrow E'_n = E_n - \frac{\epsilon^2}{2m\omega^2}, \quad E_n = \left(n + \frac{1}{2}\right) \hbar\omega$$

(as found above from perturbation theory, equation (2.26.1))

## EXAMPLE : Van der Waals Interaction

- Consider the force between two hydrogen atoms, both in the ground state, and separated by a distance  $r$  :



$$\hat{H} = \hat{H}_0 + V \quad \left\{ \begin{array}{l} \hat{H}_0 = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} \\ V = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r} + \frac{1}{|\mathbf{r} + \mathbf{r}_2 - \mathbf{r}_1|} - \frac{1}{|\mathbf{r} + \mathbf{r}_2|} - \frac{1}{|\mathbf{r} - \mathbf{r}_1|} \right) \end{array} \right.$$

## Example: Van der Waals (2)

- If the separation  $r$  is large enough, the potential  $V$  can be treated as a perturbation with respect to  $H_0$  :  
The unperturbed ground state (of  $H_0$ ) is the product of two hydrogen atom ground state wavefunctions  $|n\ell m\rangle = |100\rangle$  :

$$|0^{(0)}\rangle = |100(\mathbf{r}_1)\rangle |100(\mathbf{r}_2)\rangle ; \quad \hat{H}_0|0^{(0)}\rangle = -2R_\infty|0^{(0)}\rangle$$

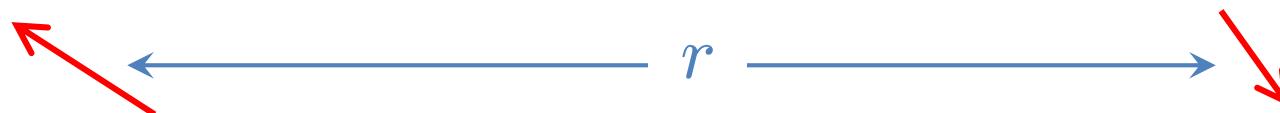
- For  $r \gg a_0$ , we can use the multipole expansion to expand the perturbation,  $H' = V$ , in powers of  $r_i/r$  :

$$V = \frac{e^2}{4\pi\epsilon_0 r^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2) + \mathcal{O}\left(\frac{1}{r^4}\right) + \dots$$

- To leading-order,  $V$  corresponds to the interaction of two electric dipoles  $e\mathbf{r}_1, e\mathbf{r}_2$  separated by a distance  $r$  :

$$\mathbf{p}_1 = e\mathbf{r}_1 = e(x_1, y_1, z_1)$$

$$\mathbf{p}_2 = e\mathbf{r}_2 = e(x_2, y_2, z_2)$$



## Example: Van der Waals (3)

- The first-order matrix elements of  $V$  all vanish (by symmetry) :

$$\langle 100|x_{1,2}|100\rangle = \langle 100|y_{1,2}|100\rangle = \langle 100|z_{1,2}|100\rangle = 0$$

Hence the first-order correction to the ground state energy vanishes also :

$$\Delta E_0^{(1)} = \langle 0^{(0)}|V|0^{(0)}\rangle = 0$$

- The first non-vanishing contribution comes at second-order :

$$\Delta E^{(2)}(r) = \left( \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^3} \right)^2 \sum_{k \neq 0} \underbrace{\frac{|\langle k^{(0)} | (x_1 x_2 + y_1 y_2 - 2z_1 z_2) | 0^{(0)} \rangle|^2}{E_0^{(0)} - E_k^{(0)}}}_{( \text{ independent of } r )}$$

- Hence the interaction varies as  $1/r^6$ , and, since  $E_0^{(0)} < E_k^{(0)}$  for all  $k$ , the interaction energy is negative (i.e. attractive)

This  $1/r^6$  long-range, attractive *van der Waals' potential* is a general feature of the interaction between two atoms in their ground state

# Degenerate Perturbation Theory

Now return to the issue with *degenerate states* left over from slide 2.9 ...

- If a pair of zeroth-order eigenstates  $|m^{(0)}\rangle$  and  $|n^{(0)}\rangle$  are degenerate in energy,  $E_m^{(0)} = E_n^{(0)}$ , then equation (2.8.2) reduces to equation (2.9.2) :

$$\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = 0 \quad (m \neq n, \quad E_m^{(0)} = E_n^{(0)})$$

Therefore, to obtain a solution to the perturbation theory equations, the unperturbed (zeroth-order) states must satisfy the condition

$$\left\{ m \neq n, \quad E_m^{(0)} = E_n^{(0)} \right\} \Rightarrow \langle m^{(0)} | \hat{H}' | n^{(0)} \rangle = 0 \quad (2.30.1)$$

- However the zeroth-order states  $|m^{(0)}\rangle$  and  $|n^{(0)}\rangle$ , and the perturbation  $H'$ , are given quantities over which we have no control, and

*there is no guarantee initially that any unperturbed states which are degenerate will satisfy condition (2.30.1)*

But all is not lost ...

## Degenerate perturbation theory (2)

- Consider an unperturbed energy level  $E_n^{(0)}$  which has degeneracy  $g > 1$  :

$$\hat{H}^{(0)}|n_j^{(0)}\rangle = E_n^{(0)}|n_j^{(0)}\rangle \quad (j = 1, 2, \dots, g)$$

- For perturbation theory to work, the unperturbed degenerate states  $|n_j^{(0)}\rangle$  must satisfy the condition on the previous slide :

$$\langle n_j^{(0)}|\hat{H}'|n_k^{(0)}\rangle = 0 \quad (j \neq k)$$

Equivalently, in the basis of states  $|n_j^{(0)}\rangle$ , the  $g \times g$  matrix representation of the operator  $H'$  must be diagonal :

$$H'_{jk} \equiv \langle n_j^{(0)}|\hat{H}'|n_k^{(0)}\rangle = E'_{n,j}\delta_{jk} \quad (2.31.1)$$
$$H' = \text{diag}(E'_{n,1}, E'_{n,2}, \dots, E'_{n,g})$$

where the  $E'_{n,j}$  are a set of constants

- The condition (2.31.1) cannot (initially) be guaranteed, but we can find *linear combinations* of the given states  $|n_j^{(0)}\rangle$  which will do the job ...

## Degenerate perturbation theory (3)

- The  $g \times g$  matrix

$$\hat{H}'_{jk} \equiv \langle n_j^{(0)} | \hat{H}' | n_k^{(0)} \rangle$$

has eigenvalues and eigenvectors given by the solutions of the equation

$$\begin{pmatrix} H'_{11} & H'_{12} & \dots & H'_{1g} \\ H'_{21} & H'_{22} & \dots & H'_{2g} \\ \vdots & \vdots & \ddots & \vdots \\ H'_{g1} & H'_{g2} & \dots & H'_{gg} \end{pmatrix} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ \vdots \\ c_{g\alpha} \end{pmatrix} = E'_{n,\alpha} \begin{pmatrix} c_{1\alpha} \\ c_{2\alpha} \\ \vdots \\ c_{g\alpha} \end{pmatrix} \quad (2.32.1)$$

where the index  $\alpha = 1, 2, \dots, g$  labels the  $g$  different solutions

- Since the operator  $H'$  is Hermitian, the matrix  $H'$  is also Hermitian  
→ the eigenvalues  $E'_{n,\alpha}$  are therefore real, and the (normalised) eigenvectors  $\mathbf{c}_\alpha$  are mutually orthonormal :

$$\mathbf{c}_\alpha \equiv (c_{1\alpha}, c_{2\alpha}, \dots, c_{g\alpha}) ; \quad \mathbf{c}_\alpha \cdot \mathbf{c}_\beta = \delta_{\alpha\beta} \quad (2.32.2)$$

## Degenerate perturbation theory (4)

-- The states

$$|n_{\alpha}^{(0)}\rangle \equiv \sum_{j=1}^g c_{j\alpha} |n_j^{(0)}\rangle \quad (\alpha = 1, 2, \dots, g)$$

corresponding to each eigenvector  $c_{\alpha}$  satisfy the equivalent of eqn (2.32.1),

$$\hat{H}' |n_{\alpha}^{(0)}\rangle = E'_{n,\alpha} |n_{\alpha}^{(0)}\rangle \quad (2.33.1)$$

They are also orthonormal, as in the equivalent of equation (2.32.2) :

$$\langle n_{\beta}^{(0)} | n_{\alpha}^{(0)} \rangle = \delta_{\alpha\beta}$$

-- Taking the inner product of equation (2.33.1) with  $\langle n_{\beta}^{(0)} |$  then shows that, in the basis  $|n_{\alpha}^{(0)}\rangle$ , the matrix representation of  $H'$  is *diagonal* :

$$\boxed{\langle n_{\beta}^{(0)} | \hat{H}' | n_{\alpha}^{(0)} \rangle = E'_{n,\alpha} \delta_{\alpha\beta}} \quad (2.33.2)$$

Thus :

*the eigenstates  $|n_{\alpha}^{(0)}\rangle$  of  $H'$  satisfy the condition (2.31.1) for the perturbation theory equations to be solvable*

## Degenerate perturbation theory (5)

- Provided we work in the zeroth-order basis  $|n_\alpha^{(0)}\rangle$ , rather than  $|n_j^{(0)}\rangle$ , all the results obtained earlier can safely be applied to degenerate states

In particular, the first-order energy corrections for each of the  $g$  degenerate states are given by equation (2.7.3) :

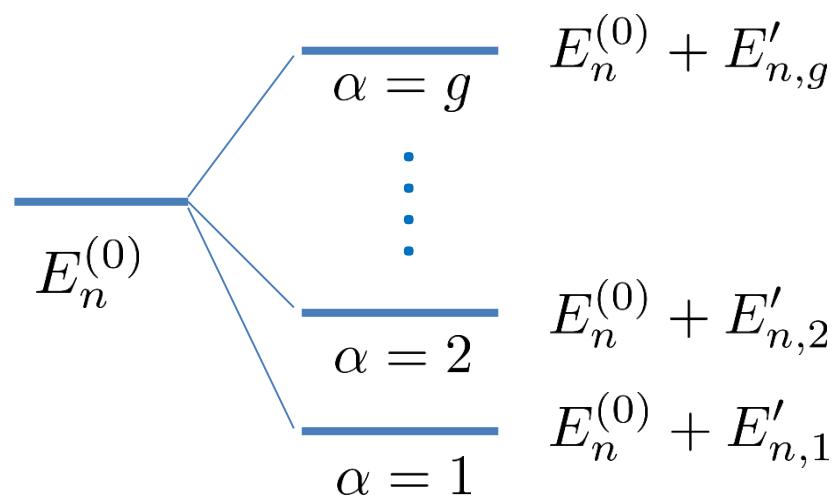
$$\Delta E_{n,\alpha}^{(1)} = \langle n_\alpha^{(0)} | \hat{H}' | n_\alpha^{(0)} \rangle \quad (\alpha = 1, 2, 3, \dots, g)$$

From equation (2.33.2), these corrections are just the eigenvalues  $E'_{n,\alpha}$  of the matrix  $H'$  :

$$\Delta E_{n,\alpha}^{(1)} = E'_{n,\alpha}$$

- In general, the eigenvalues  $E'_{n,\alpha}$  will be different for each value of  $\alpha$  :

Thus, to 1<sup>st</sup>-order, the original energy level  $E_n^{(0)}$  splits into (up to)  $g$  distinct levels in the presence of  $H'$



## Degenerate perturbation theory : Summary

- For an energy level  $n$  with degeneracy  $g > 1$ , the procedure is :
  - find the matrix representation  $\langle n_j^{(0)} | \hat{H}' | n_k^{(0)} \rangle$  of  $H'$  in the given initial basis of eigenstates  $|n_j^{(0)}\rangle$  for that energy level
  - find the eigenvalues  $E'_{n,\alpha}$  and eigenvectors  $|n_\alpha^{(0)}\rangle$  of the matrix  $H'$
- Then :
  - the  $|n_\alpha^{(0)}\rangle$  are linear combinations of the original states  $|n_j^{(0)}\rangle$  which can legitimately be used as zeroth-order states in perturbation theory (i.e. they satisfy the condition given on slide 2.30)
  - the eigenvalues  $E'_{n,\alpha}$  give the first-order energy corrections directly ; the original energy level splits into (up to)  $g$  separate levels
- Provided the states  $|n_\alpha^{(0)}\rangle$  are used as the zeroth-order states, the results obtained earlier apply to degenerate as well as to non-degenerate states

## EXAMPLE : Perturbed 2D infinite square well

- Consider a particle of mass  $m$  confined within a 2D infinite square well of dimension  $2a \times 2a$  :

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(x, y) ; \quad V(x, y) = \begin{cases} 0 & |x| < a, |y| < a \\ \infty & \text{otherwise} \end{cases}$$

- The unperturbed Hamiltonian  $H_0$  has eigenstates which are products of eigenstates  $|n_x\rangle$  and  $|n_y\rangle$  of separate 1D infinite wells for  $x$  and  $y$  :

$$|n_x, n_y\rangle = |n_x\rangle \otimes |n_y\rangle ; \quad n_x, n_y = 1, 2, 3, \dots$$

$$\psi(x, y) = \frac{1}{a} \sin\left(\frac{n_x \pi}{2a}(x + a)\right) \sin\left(\frac{n_y \pi}{2a}(y + a)\right)$$

- The unperturbed 2D energies are the sum of the two 1D energies :

$$E_{n_x, n_y}^{(0)} = (n_x^2 + n_y^2) E_0 , \quad E_0 = \frac{\hbar^2 \pi^2}{8ma^2}$$

## Example: perturbed 2D well (2)

- All states with  $n_x \neq n_y$  are degenerate, with degeneracy  $g = 2$   
e.g. the first excited state consists of the two degenerate states

$$|n_x, n_y\rangle = |1, 2\rangle, |2, 1\rangle; \quad E_{1,2}^{(0)} = E_{2,1}^{(0)} = 5E_0$$

- Now apply a perturbation

$$\hat{H}' = \epsilon xy$$

The perturbation  $\hat{H}'$  has matrix elements which factorise as

$$\langle m_x, m_y | \hat{H}' | n_x, n_y \rangle = \epsilon \langle m_x | x | n_x \rangle \langle m_y | y | n_y \rangle$$

- The factors on the RHS have already been considered on slide 2.21 :

$$\langle m_x | x | n_x \rangle = \frac{1}{a} \int_{-a}^{+a} x \sin\left(\frac{m_x \pi}{2a}(x+a)\right) \sin\left(\frac{n_x \pi}{2a}(x+a)\right) dx$$

(and similarly for  $y$ )

In particular :

$$\langle 1 | x | 2 \rangle = \frac{1}{a} \int_{-a}^{+a} x \sin\left(\frac{\pi}{2a}(x+a)\right) \sin\left(\frac{\pi}{a}(x+a)\right) dx = -\frac{32}{9} \frac{a}{\pi^2}$$

### Example: perturbed 2D well (3)

- For the first excited state, we have

$$\langle 1, 2 | xy | 2, 1 \rangle = \langle 1 | x | 2 \rangle \langle 2 | y | 1 \rangle = a^2 \left( \frac{32}{9\pi^2} \right)^2$$

- Thus the matrix representation of  $H'$  is not (initially) diagonal :

$$\langle 1, 2 | \hat{H}' | 2, 1 \rangle = \langle 2, 1 | \hat{H}' | 1, 2 \rangle = A ; \quad A = \epsilon a^2 \left( \frac{32}{9\pi^2} \right)^2$$

⇒ to apply perturbation theory, we must find suitable linear combinations of the initial states  $|1,2\rangle$  and  $|2,1\rangle$

- These are found by diagonalising the  $2 \times 2$  matrix

$$\begin{pmatrix} \langle 1, 2 | \hat{H}' | 1, 2 \rangle & \langle 1, 2 | \hat{H}' | 2, 1 \rangle \\ \langle 2, 1 | \hat{H}' | 1, 2 \rangle & \langle 2, 1 | \hat{H}' | 2, 1 \rangle \end{pmatrix} = \begin{pmatrix} 0 & A \\ A & 0 \end{pmatrix}$$

This matrix has eigenvalues  $\pm A$  and eigenvectors  $\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$

## Example: perturbed 2D well (4)

- Hence the (normalised) zeroth-order eigenstates which must be used in perturbation theory are

$$|\psi_{\pm}\rangle \equiv |1, 2\rangle_{\pm} = \frac{1}{\sqrt{2}} (|1, 2\rangle \pm |2, 1\rangle)$$

It is straightforward to check that these states do indeed diagonalise the perturbation :

$$\begin{pmatrix} \langle \psi_+ | \hat{H}' | \psi_+ \rangle & \langle \psi_+ | \hat{H}' | \psi_- \rangle \\ \langle \psi_- | \hat{H}' | \psi_+ \rangle & \langle \psi_- | \hat{H}' | \psi_- \rangle \end{pmatrix} = \begin{pmatrix} A & 0 \\ 0 & -A \end{pmatrix}$$

- The first-order energy corrections are given, with no further work, by the diagonal elements above :

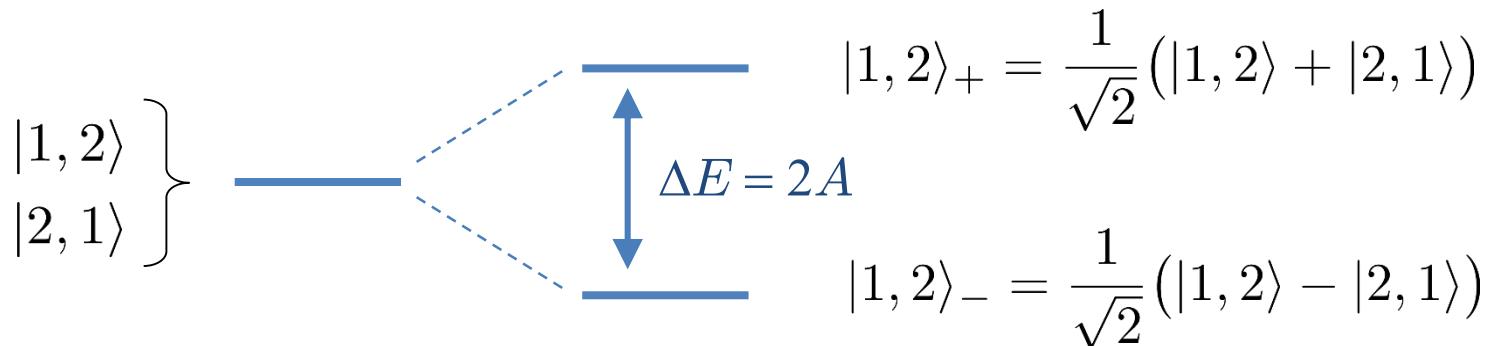
$$\Delta E^{(1)} = \langle \psi_{\pm} | \hat{H}' | \psi_{\pm} \rangle = \pm A = \pm \epsilon a^2 \left( \frac{32}{9\pi^2} \right)^2$$

## Example: perturbed 2D well (5)

- In summary, application of the perturbation

$$\hat{H}' = \epsilon xy$$

to the 2D infinite square well splits the degenerate ( $g = 2$ ) first-excited level into two separate levels :



where  $A = \epsilon a^2 \left( \frac{32}{9\pi^2} \right)^2$

- The zeroth-order states  $|1, 2\rangle_+$  and  $|1, 2\rangle_-$  could be used to compute the energy corrections and wavefunctions to any order of perturbation theory

# Perturbation Theory : Summary

- Perturbation theory applies to Hamiltonians of the form

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'$$

where the eigenvalues and eigenstates of  $\hat{H}^{(0)}$  are already known,

$$\hat{H}^{(0)}|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle ; \quad \langle n^{(0)}|m^{(0)}\rangle = \delta_{nm}$$

and where the corrections induced by the perturbation  $\hat{H}'$  are small, and where the eigenvalues  $E_n$  and eigenstates  $|n\rangle$  of the full Hamiltonian,

$$(\hat{H}^{(0)} + \hat{H}')|n\rangle = E_n|n\rangle$$

evolve smoothly away from the unperturbed eigenvalues and eigenstates

- For a given unperturbed eigenstate  $|n^{(0)}\rangle$  of energy  $E_n^{(0)}$ , the perturbed energy, up to second-order, is given by

$$E_n = E_n^{(0)} + \langle n^{(0)}|\hat{H}'|n^{(0)}\rangle + \sum_{E_m^{(0)} \neq E_n^{(0)}} \frac{|\langle m^{(0)}|\hat{H}'|n^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}} + \dots$$

## Perturbation theory : Summary (2)

- To first-order, the perturbed eigenstate is given by

$$|n\rangle = |n^{(0)}\rangle + \sum_{E_m^{(0)} \neq E_n^{(0)}} |m^{(0)}\rangle \frac{\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} + \dots$$

- If the energy level  $E_n^{(0)}$  is degenerate ( $g > 1$ ), the results above apply provided the procedure summarised on slide 2.35 has been followed
  - the states  $|n^{(0)}\rangle$  must be taken to be the states  $|n_\alpha^{(0)}\rangle$ , rather than the states  $|n_j^{(0)}\rangle$  (and similarly for the states  $|m^{(0)}\rangle$ )
- The procedure on slide 2.35 amounts to diagonalising the perturbation  $H'$  within each degenerate energy level, by solving the secular equation

$$\det(H'_{jk} - E' \delta_{jk}) = 0 \quad (j, k = 1, 2, \dots, g)$$

The solutions  $E'$  directly provide the first-order energy corrections for the degenerate level, without further work

# *The Variational Method*

- The *variational method* provides an estimate of (strictly, an *upper bound* on) the eigenstate energies of any given Hamiltonian  $H$   
(including Hamiltonians for which perturbation theory is inapplicable)
- The method is based on guessing, then optimising, a *trial wavefunction*  $\Psi_{\text{trial}}(\alpha_i)$  which depends on one or more *variational parameters*  $\alpha_i$

The optimisation involves minimising the expectation value of the energy

$$E(\alpha_i) = \min_{\alpha_i} \langle \psi_{\text{trial}}(\alpha_i) | \hat{H} | \psi_{\text{trial}}(\alpha_i) \rangle$$

with respect to the parameters  $\alpha_i$

This is a seemingly crude approach, but one that can nevertheless provide a surprisingly good approximation to the true energy

- We will consider only the *ground state* of the Hamiltonian  $H$  ; the method can be extended to excited states also

## The variational method (2)

- Consider a Hamiltonian  $H$  with unknown eigenstates and energies :

$$\hat{H}|n\rangle = E_n|n\rangle$$

- Introduce a normalised trial state  $|\psi(\alpha)\rangle$  which is a function of a set of parameters  $\alpha$  and can be expanded in terms of the complete set of states  $|n\rangle$  :

$$|\psi(\alpha)\rangle = \sum_n a_n(\alpha)|n\rangle ; \quad \sum_n |a_n(\alpha)|^2 = 1$$

- The expectation value for the energy in the state  $|\psi(\alpha)\rangle$  is

$$E(\alpha) \equiv \langle\psi(\alpha)|\hat{H}|\psi(\alpha)\rangle = \sum_n |a_n(\alpha)|^2 E_n$$

- Since (by definition) the ground state energy  $E_0 \leq E_n$  for all  $n$ , we have

$$E(\alpha) \geq E_0 \sum_n |a_n(\alpha)|^2 = E_0$$

- Thus, for all values of the parameters  $\alpha$ ,  $E(\alpha)$  places an *upper bound* on the energy  $E_0$  :

$$E(\alpha) \equiv \langle\psi(\alpha)|\hat{H}|\psi(\alpha)\rangle \geq E_0$$

## The variational method (3)

- The tightest possible upper bound on the ground state energy  $E_0$  is found by minimising the function  $E(\alpha)$  with respect to the parameters  $\alpha$  :

$$E_0 \leq \min_{\alpha} \frac{\langle \psi(\alpha) | \hat{H} | \psi(\alpha) \rangle}{\langle \psi(\alpha) | \psi(\alpha) \rangle}$$

where the denominator is included in case the trial wavefunction has not already been explicitly normalised

- The trial wavefunction  $\psi(\alpha)$  can usually be chosen to be a rather general, convenient function of the parameters  $\alpha$  :
  - it should be chosen to satisfy any relevant symmetry properties and boundary conditions
  - the closer it is to the true (but unknown) ground state wavefunction, the closer the minimum will be to the true ground state energy

## The variational method (4)

- Even a poor choice of trial wavefunction can provide a surprisingly good estimate of the ground state energy :
  - e.g. suppose the optimised trial wavefunction contains a 20% admixture of the true first excited state :

$$|\psi(\alpha_0)\rangle = \frac{1}{\sqrt{1 + (0.2)^2}} (|0\rangle + 0.2|1\rangle)$$

where  $|0\rangle$  is the true ground state, i.e. the true answer

- The estimate of the true ground state energy will then be too high by only

$$\delta E = \frac{E_0 + (0.2)^2 E_1}{1 + (0.2)^2} - E_0 = \frac{(0.2)^2}{1 + (0.2)^2} (E_1 - E_0)$$

- i.e. the estimate is too high by only about 4% of the energy gap  $\Delta E = E_1 - E_0$  between the ground and first-excited states

## EXAMPLE : Hydrogen atom ground state energy

- For the zeroth-order hydrogen atom, the Hamiltonian is

$$\hat{H} = \frac{1}{2m_e} \hat{\mathbf{p}}_e^2 - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

- Choose a trial wavefunction containing a single variational parameter  $\beta$ , with (unnormalised) form

$$\psi(\mathbf{r}) = e^{-\beta r}$$

$[\psi(r) \rightarrow 0 \text{ as } r \rightarrow \infty]$

- The expectation value of the energy for the trial wavefunction is

$$\langle \psi | \hat{H} | \psi \rangle = -\frac{\hbar^2}{2m_e} \langle \psi | \nabla^2 | \psi \rangle - \frac{e^2}{4\pi\epsilon_0} \langle \psi | \frac{1}{r} | \psi \rangle$$

- Since  $\psi$  depends only on the radius  $r$ , we have

$$\nabla^2 \psi = \left( \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \right) e^{-\beta r} = -\beta \left( \frac{2}{r} - \beta \right) e^{-\beta r}$$

## Example : H atom ground state energy (2)

-- Hence

$$\langle \psi | \nabla^2 | \psi \rangle = -2\beta \langle \psi | (1/r) | \psi \rangle + \beta^2 \langle \psi | \psi \rangle$$

$$\langle \psi | \frac{1}{r} | \psi \rangle = \int_0^\infty \frac{1}{r} |\psi(r)|^2 4\pi r^2 dr = 4\pi \int_0^\infty r e^{-2\beta r} dr = \frac{\pi}{\beta^2}$$

$$\langle \psi | \psi \rangle = \int_0^\infty |\psi(r)|^2 4\pi r^2 dr = 4\pi \int_0^\infty r^2 e^{-2\beta r} dr = \frac{\pi}{\beta^3}$$

-- Putting it all together (and accounting for normalisation) :

$$E(\beta) \equiv \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\hbar^2}{2m_e} \beta^2 - \frac{e^2}{4\pi\epsilon_0} \beta$$

-- This has a minimum (at  $\beta = \beta_0$ ) when

$$\frac{dE}{d\beta} = \frac{\hbar^2 \beta}{m_e} - \frac{e^2}{4\pi\epsilon_0} = 0 \quad \Rightarrow \quad \beta_0 = \frac{e^2}{4\pi\epsilon_0} \frac{m_e}{\hbar^2}$$

## Example : H atom ground state energy (3)

- The minimum value of the energy is

$$E(\beta_0) = \frac{\hbar^2}{2m_e} \beta_0^2 - \frac{e^2}{4\pi\epsilon_0} \beta_0 = - \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{1}{2} m_e c^2$$

- This gives an upper bound on the true ground state energy  $E_0$  :

$$E_0 \leq - \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{1}{2} m_e c^2 = -R_\infty \approx -13.6 \text{ eV}$$

- This bound is, in fact, the same as the true answer, because the true ground state wavefunction

$$\psi(\mathbf{r}) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

is of the same form as that chosen for the trial wavefunction

# The Rayleigh-Ritz Method

- The *Rayleigh-Ritz method* is a particular example of the variational method which employs a trial wavefunction of the form

$$\psi(\mathbf{r}) = \sum_j \alpha_j \psi_j(\mathbf{r})$$

where the  $\psi_j$  are a linearly independent set of wavefunctions, the  $\alpha_j$  are treated as variational parameters, and

*the states  $\psi_j$  do not necessarily have to be complete or orthonormal*

- For example, in molecular physics, states can be approximated as a linear combination of single-electron atomic states
  - *Linear Combination of Atomic Orbitals (LCAO)*

The Rayleigh-Ritz method can then be used to determine the optimal linear combination

## The Rayleigh-Ritz method (2)

- The quantity to be minimised is the expectation value

$$\langle E \rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\sum_{j,k} \alpha_j \alpha_k \langle \psi_j | \hat{H} | \psi_k \rangle}{\sum_{j,k} \alpha_j \alpha_k \langle \psi_j | \psi_k \rangle} \equiv \frac{\sum_{j,k} \alpha_j \alpha_k H_{jk}}{\sum_{j,k} \alpha_j \alpha_k S_{jk}} \quad (2.51.1)$$

where the constants  $H_{jk}$  and  $S_{jk}$  are defined as

$$H_{jk} \equiv \langle \psi_j | \hat{H} | \psi_k \rangle = H_{kj}^* ; \quad S_{jk} \equiv \langle \psi_j | \psi_k \rangle = S_{kj}^*$$

- Minimising  $\langle E \rangle$  with respect to the variational parameter  $\alpha_i$  gives

$$0 = \frac{\partial \langle E \rangle}{\partial \alpha_i} = \frac{\sum_k \alpha_k H_{ik} + \sum_j \alpha_j H_{ji}}{\sum_{j,k} \alpha_j \alpha_k S_{jk}} - \frac{\sum_{j,k} \alpha_j \alpha_k H_{jk}}{\left( \sum_{j,k} \alpha_j \alpha_k S_{jk} \right)^2} \left( \sum_k \alpha_k S_{ik} + \sum_j \alpha_j S_{ji} \right) \quad \left( \frac{\partial \alpha_j}{\partial \alpha_i} = \delta_{ij} , \quad \frac{\partial \alpha_k}{\partial \alpha_i} = \delta_{ik} \right)$$

## The Rayleigh-Ritz method (3)

- This tidies up (for each value of the index  $i$ ) as

$$\begin{aligned} & \left( \sum_k \alpha_k (H_{ik} + H_{ki}) \right) \left( \sum_{j,k} \alpha_j \alpha_k S_{jk} \right) \\ &= \left( \sum_k \alpha_k (S_{ik} + S_{ki}) \right) \left( \sum_{j,k} \alpha_j \alpha_k H_{jk} \right) \end{aligned}$$

- We shall only need to consider the case that the  $H_{jk}$  and  $S_{jk}$  are both real matrices; the equation above then simplifies (for each  $i$ ) as

$$\left( \sum_k \alpha_k H_{ik} \right) \left( \sum_{j,k} \alpha_j \alpha_k S_{jk} \right) = \left( \sum_k \alpha_k S_{ik} \right) \left( \sum_{j,k} \alpha_j \alpha_k H_{jk} \right) \quad (2.52.1)$$

- If the minimum value of  $\langle E \rangle$  is  $\langle E \rangle = E_{\min}$ , then, from equation (2.51.1), we also have

$$\left( \sum_{j,k} \alpha_j \alpha_k S_{jk} \right) E_{\min} = \left( \sum_{j,k} \alpha_j \alpha_k H_{jk} \right) \quad (2.52.2)$$

## The Rayleigh-Ritz method (4)

- Comparing equations (2.52.1) and (2.52.2), the minimum corresponds to

$$\sum_k \alpha_k (H_{ik} - E_{\min} S_{ik}) = 0 \quad (\text{for each } i)$$

- This represents a set of simultaneous equations for the  $\alpha_i$ , which can be written in matrix form as

$$(H - E_{\min} S)\alpha = 0$$

- Non-trivial solutions are obtained by solving the secular equation

$$\det(H - E_{\min} S) = 0$$

The lowest of the resulting set of eigenvalues  $E_{\min}$  provides the best upper bound on the ground state energy

## EXAMPLE : Hydrogen atom with finite proton mass

- A finite proton mass  $m_p$  can be taken into account exactly by replacing the electron mass  $m_e$  by the reduced mass  $\mu$  :

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} ; \quad \mu = \frac{m_p m_e}{m_p + m_e} \approx (0.999456)m_e$$

The hydrogen atom ground state energy thus becomes

$$E_0 = - \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 \frac{1}{2} \mu c^2 = - \frac{\mu}{m_e} R_\infty \approx -(0.999456)R_\infty$$

- To test / demonstrate the Rayleigh-Ritz method, we consider the same problem using a trial wavefunction of the form

$$\psi_{\text{trial}} = \alpha_1 |100\rangle + \alpha_2 |200\rangle$$

which is a linear combination of *infinite-mass states*  $|nlm_\ell\rangle$

i.e. the wavefunctions  $|100\rangle$  and  $|200\rangle$  are expressed in terms of  $m_e$  , *not* the reduced mass  $\mu$

## Example: finite proton mass (2)

-- Thus

$$\left. \begin{aligned} |100\rangle &= \left( \frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0} \\ |200\rangle &= \left( \frac{1}{32\pi a_0^3} \right)^{1/2} e^{-r/2a_0} \left( 2 - \frac{r}{a_0} \right) \end{aligned} \right\} a_0 = \frac{4\pi\epsilon_0}{e^2} \frac{\hbar^2}{m_e}$$

-- In this case, the basis states happen to be orthonormal :

$$S_{jk} \equiv \langle \psi_j | \psi_k \rangle ; \quad S_{11} = S_{22} = 1 ; \quad S_{12} = S_{21} = 0$$

-- The Hamiltonian matrix elements are given by

$$H_{jk} \equiv \langle \psi_j | \hat{H} | \psi_k \rangle = \int \psi_j^* \left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_k d^3r$$

e.g.

$$H_{21} = A \int_0^\infty e^{-r/2a_0} \left( 2 - \frac{r}{a_0} \right) \left[ \left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) e^{-r/a_0} \right] 4\pi r^2 dr$$

where  $A = \left( \frac{1}{32\pi a_0^3} \right)^{1/2} \left( \frac{1}{\pi a_0^3} \right)^{1/2} = \frac{1}{\sqrt{32} \pi a_0^3}$

### Example: finite proton mass (3)

-- Using

$$\nabla^2 e^{-\beta r} = \left( \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \right) e^{-\beta r} = -\beta \left( \frac{2}{r} - \beta \right) e^{-\beta r} ; \quad \beta \equiv \frac{1}{a_0}$$

$$\int_0^\infty r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}$$

gives

$$H_{11} = 4H_{22} = \left( \frac{m_e}{m_p} - 1 \right) R_\infty ; \quad H_{12} = H_{21} = \frac{16}{27\sqrt{2}} \frac{m_e}{m_p} R_\infty$$

-- The secular equation is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$\Rightarrow E^2 - (H_{11} + H_{22})E + H_{11}H_{22} - H_{12}H_{21} = 0$$

$$\Rightarrow E = - \left( 1 - \frac{m_e}{m_p} \right) \left[ \frac{5}{8} \pm \frac{3}{8} \sqrt{1 + 2 \left( \frac{64}{81} \frac{m_e}{m_p - m_e} \right)^2} \right] R_\infty$$

## Example: finite proton mass (4)

- The best (lowest) upper bound is obtained by choosing the “+” sign :

$$E_{\min} \approx -(0.999455)R_{\infty}$$

which is within 3 parts in  $10^7$  of the true answer

- The ground-state wavefunction corresponding to this minimum is found by solving

$$\begin{pmatrix} H_{11} - E_{\min} & H_{12} \\ H_{21} & H_{22} - E_{\min} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = 0$$

This gives

$$\frac{\alpha_1}{\alpha_2} = -\frac{H_{12}}{H_{11} - E_{\min}} \approx -3284.7$$

- Requiring also  $\alpha_1^2 + \alpha_2^2 = 1$  then fixes

$$\alpha_1 \approx 0.999999954, \quad \alpha_2 \approx -0.000304$$

i.e. with a finite-mass proton, the ground-state wavefunction contains about a 3 parts in  $10^4$  admixture of the infinite-mass 2s wavefunction

# Appendix : Second-order Perturbation Theory

- For completeness, we obtain the expression of the second-order energy correction,  $E_n^{(2)}$ , of equation (2.13.1), in a way which demonstrates explicitly that  $E_n^{(2)}$  does not depend on any indeterminate overlaps
- We start from the “master equation” for second-order perturbation theory given in equation (2.12.1) :

$$\hat{H}^{(0)}|n^{(2)}\rangle + \hat{H}^{(1)}|n^{(1)}\rangle = E_n^{(0)}|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n^{(0)}\rangle$$

- Taking the inner product with  $\langle n^{(0)}|$  , and cancelling the first terms on each side, leaves

$$\langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle = E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle + E_n^{(2)} \quad (2.58.1)$$

- The first-order correction  $|n^{(1)}\rangle$  can be expanded in terms of the unperturbed states as in equation (2.8.1) :

$$|n^{(1)}\rangle = \sum_m \langle m^{(0)}|n^{(1)}\rangle |m^{(0)}\rangle \quad (2.58.2)$$

## Appendix : Second-order perturbation theory (2)

- Separating out explicitly the  $m = n$  term, and the terms involving states degenerate in energy with  $|n^{(0)}\rangle$ , equation (2.58.2) can be written as

$$|n^{(1)}\rangle = \underbrace{\langle n^{(0)}|n^{(1)}\rangle|n^{(0)}\rangle}_{(m=n)} + \underbrace{\sum_{E_m^{(0)}=E_n^{(0)}} \langle m^{(0)}|n^{(1)}\rangle|m^{(0)}\rangle}_{(m \neq n)} + \sum_{E_m^{(0)} \neq E_n^{(0)}} \langle m^{(0)}|n^{(1)}\rangle|m^{(0)}\rangle \quad (2.59.1)$$

The overlaps appearing in the first two terms on the right-hand side above cannot be unambiguously determined

- Substituting the expression for  $|n^{(1)}\rangle$  of equation (2.59.1) into the matrix element on the left-hand side of equation (2.58.1) gives

$$\begin{aligned} & \langle n^{(0)}|n^{(1)}\rangle\langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle + \sum_{E_m^{(0)}=E_n^{(0)}} \langle m^{(0)}|n^{(1)}\rangle\langle n^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle \\ & + \sum_{E_m^{(0)} \neq E_n^{(0)}} \langle m^{(0)}|n^{(1)}\rangle\langle n^{(0)}|\hat{H}^{(1)}|m^{(0)}\rangle = E_n^{(1)}\langle n^{(0)}|n^{(1)}\rangle + E_n^{(2)} \end{aligned} \quad (2.59.2)$$

## Appendix : Second-order perturbation theory (3)

- From equation (2.7.2), we have  $E_n^{(1)} = \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle$ ; hence the terms in equation (2.59.2) containing the indeterminate overlap  $\langle n^{(0)} | n^{(1)} \rangle$  cancel
- Degenerate states can always be arranged to satisfy equation (2.9.2) :

$$\langle m^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle = 0 \quad (E_m^{(0)} = E_n^{(0)})$$

Hence equation (2.59.2) simplifies as

$$E_n^{(2)} = \sum_{E_m^{(0)} \neq E_n^{(0)}} \langle m^{(0)} | n^{(1)} \rangle \langle n^{(0)} | \hat{H}^{(1)} | m^{(0)} \rangle$$

This is equation (2.12.2) again

- Hence, as before, we obtain equation (2.13.1), but now without choosing any particular value (such as zero) for the indeterminate overlaps :

$$\boxed{\Delta E_n^{(2)} = \lambda^2 E_n^{(2)} = \sum_{E_m^{(0)} \neq E_n^{(0)}} \frac{|\langle m^{(0)} | \hat{H}' | n^{(0)} \rangle|^2}{E_n^{(0)} - E_m^{(0)}}}$$