## Introduction, Exact Results, the Variational Principle and Hückel Theory

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January 14, 2015

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Force-fields (equivalent term: potentials) are commonly used in simulations. These are generally fine, but may sometimes lead to insufficiently precise, or even qualitatively wrong results. Here are popular choices:

$$V_{
m LJ}(r_{ij}) = rac{A}{r_{ij}^{12}} - rac{C}{r_{ij}^6}$$
 $V_{
m exp6}(r_{ij}) = e^{-lpha(r_{ij}-
ho_{ij})} - rac{C_6^{ij}}{r_{ij}^6} + rac{q_i q_j}{r_{ij}}$ 

- 'spherical' atoms
- simple electrostatic models
- 'static' potentials

How do we go beyond the limitations of empirical potentials?

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Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory

#### Are point-charges good enough?



**Figure 4.** Distributions of  $\Delta E$  with the atomic point charge and atomic multipole models.

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From Day et al. (2005).

Approximate Methods

Hückel Theory

### Point charges?: Metal-organic frameworks.





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Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory

### Are atoms spherical?







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Hückel Theory

Going beyond static potentials: In systems with strong permanent moments and polarizabilities (water is a good example) the effects of *polarization* can be very important. This introduces a dynamical effect to the potential: it now needs to respond to the *environment*.





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Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory





Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory

So we might want to use *many-body* potentials of the form:

$$V_{MB}(r_{ij}) = e^{-\alpha(r_{ij} - \rho_{ij}(\Omega))} - f_6(\beta r_{ij}) \frac{C_6^{ij}}{r_{ij}^6} - f_8(\beta r_{ij}) \frac{C_8^{ij}}{r_{ij}^8} \cdots + Q_{lm}^i T_{lm,l'm'}^{lj} Q_{l'm'}^j + \{\alpha_{lm,l'm'}^i, Q_{lm}^i, \forall i\}$$

Q: Where do we get the data to develop all these extra terms? Q: How do we account for bond-breaking and many-body charge transfer?

Q: What about correlation in semi-metallic systems with plasmon modes?

Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory

Other reasons for *ab initio* data:

- Comformations used by complex molecules
- Bond-making/breaking
- No experimental data available to parameretize potentials in region of phase-space (simulations of matter under extreme or unusual conditions (see next example).
- Complex electronic excitations coupled with dymanics: charge (electron or proton) transfer. Lots of chaps in UCL doing this sort of thing theoretically and a number here in QM studying such processes experimentally.



Matter under extreme conditions: Ab initio random structure searching (AIRSS) of Chris Pickard and Richard Needs.



Figure 2 (Hele-part Houlzman, J. The ATB for the part structure pickness field in a site of the part of hims, as obtained from density functional interpart of a chaldrains. The part of the category in the part of the category in the part of the part of hims, as obtained from density A. A detaches obtained from in order instances stratefield, with interpart of the part of th



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- Single-determinant methods: Hartree–Fock (HF), Density functional theory (DFT), Moller-Plesset perturbation theory at various orders (MP2, MP3, MP4,...), Configuration interaction (CI), Coupled-cluster methods (CCSD, CCSD(T), CCSDT,...), Full-configuration interaction (FCI)
  - Multi-configutation methods: MCSCF, MRCI, ...
  - Basis sets: STO-3G, 6-31G, 6-31G\*, aug-cc-pVDZ, aug-cc-pVTZ, ...
  - Programs: Castep, DALTON, NWChem, ADF, Molpro, Gaussian, Onetep, CamCASP, SAPT2008,...
- Q: What do all of these mean?
- Q: How do we choose the appropriate method/basis/program?

## Electronic structure methods II

- Properties of the exact wavefunctions
- The Variational Method
  - Hückel Theory (Tight-Binding)
- Second-Quantization
- Survey of wavefunction methods with simple examples.
- Hartree–Fock (HF) Theory
- Post-HF methods: CI, CC, MBPT
- Density-Functional Theory (DFT)
  - Failures of DFT: van der Waals
  - Failures of DFT: Charge-Transfer
- Intermolecular perturbation theory
- Fixes for DFT

## Electronic structure methods III

- We will study all of these topics while exploring them numerically using the NWCHEM and CAMCASP programs.
- Our aim will be to apply these techniques to a variety of systems, in particular the ammonia monohydrate system: our goal will be to develop a deep understanding of these methods in the context of a recent research article: *High pressure ionic and molecular crystals of ammonia*

*monohydrate within density functional theory*, G. I. G. Griffiths, A. J. Misquitta, A. D. Fortes, C. J. Pickard and R. J. Needs, J. Chem. Phys, *137*, 064506 (2012).

• You will be given other papers during the course.

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## Electronic structure methods IV

Marking:

- Homework: 20%. Will be given weekly and collected the following week. Important problems will be discussed in the class.
- Report: 20% of your mark will be based on a report written on calculations for this system. We will develop and motivate these calculations as we go along.
- Exam: 60% of your mark will be a written exam.

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## Electronic structure methods V

References:

- *Molecular Electronic Structure Theory*, Helgaker, Olsen, Jorgensen.
- Modern Quantum Chemistry, Szabo & Ostlund.
- Density functional theory of atoms and molecules, Parr and Yang
- Time-dependent density functinal theory, Carsten Ulrich

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## Electronic structure methods VI

Class preparation:

- Homework: You will be expected to come up and solve problems!
- YouTube: I will assign YouTube lectures prepared by colleagues. You will be expected to watch these. Some of the class discussions will be based on these movies.
- Reading assignments: These will be mainly from the book by Szabo & Ostlund.

We are going to be dealing with many-body (i.e., many electron) wavefunctions. So we will begin by looking at what we know about these wavefunctions and what tools we have to analyse them:

- Properties of Ψ: All the exact properties the wavefunction (and density) are expected to satisfy. Afterall, any approximate wavefunction should satisfy as many of these as is practically possible.
- Methods for approximating the wavefunction. We cannot solve much beyond the 1-electron, hydrogen atom. For anything more complex, we must solve the Schrödinger equation approximately.
- Mathematical methods: We will need some advanced mathematical methods in this course.

Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory
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Atomic units will be used throughout: effectively  $\hbar = 1$ ,  $m_{\rm e} = 1$ , e = 1.

- Mass: Has units of free-electron mass m. SI value is 9.10938  $\times$  10^{-31} kg.
- Charge: Has units of absolute value of free-electron charge *e*. SI value is  $1.60218 \times 10^{-19}$  C.
- Angular momentum: Units of reduced Planck's constant  $\hbar.$  SI value is 1.05457  $\times$  10^{-34} J s.
- Length: Units of Bohr radius of the H atom,  $a_0 = 4\pi\epsilon_0\hbar^2/me^2$ . SI value 5.29177 × 10<sup>-11</sup> m.

In these units  $c = \alpha^{-1} = 1/137.036$ , where the fine structure constant is defined as  $\alpha = e^2/4\pi\epsilon_0\hbar c$ .

Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory
Properties	ofΨII			

Notation:

- $\bullet~|\Psi\rangle$  : exact many-body wavefunction
- $\bullet~|0\rangle$  : approximate wavefunction

Our goal here is to list properties satisfied by  $|\Psi\rangle$  that we'd also like  $|0\rangle$  to satisfy. Some will be obvious, others not so obvious...

### $|\Psi\rangle$ contains N electrons:

We definitely want  $|0\rangle$  to describe the same number of electons and so expect that, if  $\hat{N}$  is a number operator (more on these when we cover second-quantization), then

$$\hat{N}|0
angle = N|0
angle$$

i.e.,  $|0\rangle$  is an eigenstate of the number operator with eigenvalue *N*. This is not normally an issue and is made explicit when we define the wavefunction in second-quantized form (more on this later).

Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory
Properties	s of Ψ IV			

Antisymmetry

$$\hat{P_{ij}}|\Psi
angle=-|\Psi
angle$$

We expect  $|0\rangle$  to be antisymmetric.

- In second-quantization (which we will use), the Pauli principle is built into the anticommutating relations of the creation/annihilation operators.
- In first-quantization, we need to make the wavefunction antisymmetric by expressing it as a linear combination of Slater determinants.

Why ab initio?	Outline	Proofs and Results	Approximate Methods	Hückel Theory
Properties	s of Ψ V			

Square-integrability of the bound states.

 $\langle \Psi | \Psi \rangle = 1$ 

To ensure that  $|0\rangle$  will always satisfy this we expand it in a basis of normalized orbitals. These orbitals will be, in turn, expanded in a basis of Gaussian-type orbitals (GTOs). These orbitals are, by definition, square-integrable.

### Properties of $\Psi$ VI

Variational stability

For all possible variations  $\delta \Psi$ , s.t.,  $\langle \delta \Psi | \Psi \rangle = 0$  (i.e., the variations are orthogonal to  $\Psi$ ),

$$\langle \delta \Psi | \hat{H} | \Psi \rangle = E \langle \delta \Psi | \Psi \rangle = 0,$$

i.e.,  $\Psi$  is stable to these variations to first order. We will define  $|0\rangle$  s.t. this principle is preserved. But not all methods gaurantee variational stability.

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Propertie	s of Ψ VII			

Asymptotic form of  $|\Psi\rangle$ :

$$\Psi \to \Psi_{N-1} e^{-\sqrt{2E_I}r},$$

where  $E_I = E_{N-1} - E_N$  is the vertical first ionisation energy of the system.

This result holds for any bound state. It is quite difficult to satisfy as the slow decay of the exponential function can be only approximately modelled by GTOs.

### The electron-nuclear cusp condition:

The Hamiltonian has a singularity in the electon–nuclear potential, however the energy of a bound state is finite. So this singularity must be cancelled by another singularity of the opposite sign. This is possible if the wavefunction has a cusp at the nuclei:

$$\left.\frac{\partial\Psi}{\partial r_{i\alpha}}\right|_{r_{i\alpha}=0}=-Z_{\alpha}\Psi(r_{i\alpha}=0)$$

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#### The electron-electron cusp condition:

For similar reasons, there must be cusps in the wavefunction when two electrons are at the same location. In this case, the cusp condition depends on the electronic spins. For a singlet system (electrons with opposite spins) we have

$$\left.\frac{\partial\Psi}{\partial r_{ij}}\right|_{r_{ij}=0}=+\frac{1}{2}\Psi(r_{ij}=0)$$

While for a triplet, we get a +1/4 on the R.H.S. This condition is responsible for correlation effects at short-range.

### Size-Extensivity

For a system containing non-interacting subsystems, the total energy is equal to the sum of energies of the individual subsystems. Consider the total Hamiltonian:

$$H_T = \sum_i^M H_i,$$

where the  $H_i$  are the Hamiltonians of non-interacting systems. If we have  $H_T \Psi_T = E_T \Psi_T$ , then we must have

$$E_T = \sum_i^M E_i,$$

where  $H_i \Psi_i = E_i \Psi_i$ .

Q: What happens is this property is violated?

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#### Spin

In non-relativistic theory, the exact stationary eigenstates of  $\hat{S}^2$  and  $\hat{S}_z$ :

$$\hat{S}^2 \Psi = S(S+1) \Psi \ \hat{S}_z \Psi = M \Psi$$

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Reminder: Atomic units used throughtout!

#### The Born–Oppenheimer approximation

We have electrons and nuclei in our general Hamiltonian. The nuclei complicate matters. But we can simplify life by arguing that since the nuclei are nearly 2000 times heavier than the electrons, they can be considered fixed while we solve the electronic Hamiltonian. That is we solve

$$\mathcal{H}_{\rm e}\Psi_{\rm e} = \mathcal{E}_{\rm e}\Psi_{\rm e} \tag{1}$$

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where

$$\mathcal{H}_{\rm e} = -\sum_{i} \frac{1}{2} \nabla_i^2 - \sum_{i} \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{i} \sum_{j>i} \frac{1}{r_{ij}}$$
(2)

to get the wavefunction and energy that will be parametrically dependent on the positions of the nuclei:

$$\Psi_{\mathrm{e}} = \Psi_{\mathrm{e}}(\{r_i\};\{R_{\alpha}\})$$
  
 $E_{\mathrm{e}} = E_{\mathrm{e}}(\{R_{\alpha}\})$ 

From the latter we get our notion of an energy landscape on which the nuclei move (often assumed to be Classically using Newtons Laws - i.e, Molecular Dynamics).

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### Properties of $\Psi$ XIV

There are two cases then the BO approximation is invalid:

- Fast nuclei: The BO condition should not really be stated in terms of the mass ratios of the electrons and nuclei, but rather in terms of the kinetic energy ratios. If nuclei are very fast, they can have kinetic energies comparable with those of the electrons. Example: Radiation damage.
- Level crossing: This is a subtle one. If two electronic energy levels cross (often happens with excited states) then if there is a vibrational mode of appropriate symmetry, the BO approximation breaks down. This is the Jahn–Teller effect where we must consider a coupling of the electronic and nuclear motions.

We will henceforth always use the electronic Hamiltonian and wavefunction.

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# Asymptotic form of $|\Psi\rangle~$ I

Proof of the asymptotic form of the density/wavefunction:

$$\Psi 
ightarrow \Psi_{N-1} e^{-\sqrt{2E_I}r},$$
 $ho(r) 
ightarrow e^{-2\sqrt{2E_I}r},$ 

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# Asymptotic form of $|\Psi\rangle~$ II

We begin this proof by first proving a simpler result for a 1-electron system. Consider the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 + V(\mathbf{r})$$

$$1 \cdot \partial^2 = 2 \cdot \partial = \hat{l}^2 \quad (3)$$

$$= -\frac{1}{2}\left(\frac{1}{\partial r^2} + \frac{1}{r}\frac{1}{\partial r} + \frac{1}{r^2}\right) + V(\mathbf{r}).$$
(4)

# Asymptotic form of $|\Psi\rangle~$ III

Now, as  $r \to \infty$ , assuming  $V(r) \to 0$  (valid for all reasonable potentials, apart for constant shifts which can be absorbed into the energy), only the first term in the above Hamiltonian survives and the eigenvalue problem reduces to

$$-\frac{1}{2}\frac{\partial^2}{\partial r^2}\psi(r) = E\psi(r).$$
(5)

The solution of this equation is the asymptotic 1-electron wavefunction, thus

$$\psi(r) \to c e^{-\sqrt{-2E}r}.$$
 (6)

For the H atom,  $E_0 = -\frac{1}{2}$  giving  $\psi_0 \rightarrow e^{-r}$ .

# Asymptotic form of $|\Psi\rangle$ IV

The N-electron case:

$$\hat{H}\Psi_N(1,2,...,N) = E_N\Psi_N(1,2,...,N)$$
(7)

As we pull one electron out,  $\Psi_N$  collapses into the state  $\Psi_{N-1}\phi(r)$ — that is, the product on an N-1-electron wavefunction and a 1-electron wavefunction  $\phi(r)$ . It is the latter that determines the asymptotic properties of  $\Psi_N$ .

We will make the assumption that the interaction terms in  $\hat{H}$  that act between  $\Psi_{N-1}$  and  $\phi(r)$  can be neglected. This is valid if the electronic state  $\Psi_{N-1}$  is sufficiently compact. This results in the separable Hamiltonian:

$$\hat{H} = \hat{H}_{N-1} + \hat{H}_1. \tag{8}$$

# Asymptotic form of $|\Psi\rangle~V$

#### Therefore

$$E_{N}\Psi_{N} = \hat{H}\Psi_{N} = (\hat{H}_{N-1} + \hat{H}_{1})\Psi_{N-1}\phi(r)$$
(9)  
=  $E_{N-1}\Psi_{N-1}\phi(r) + \Psi_{N-1}(\hat{H}_{1}\phi(r)).$ (10)

$$\Psi_{N-1}(\hat{H}_1\phi(r)) = (E_N - E_{N-1})\Psi_{N-1}\phi(r).$$
(11)

On integrating out  $\Psi_{N-1}$  we get the 1-electron eigenvalue problem:

$$\hat{H}_1\phi(r) = (E_N - E_{N-1})\phi(r).$$
 (12)

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# Asymptotic form of $|\Psi\rangle$ VI

Using the result for the 1-electron case (Eq. (6)) we get

$$\phi(\mathbf{r}) \to e^{-\sqrt{-2(E_N - E_{N-1})}\mathbf{r}}$$
(13)

$$\rightarrow e^{-\sqrt{2E_I}r},$$
 (14)

where  $E_I = E_{N-1} - E_N$  is the vertical ionization potential. This will prove a useful result in our analysis of density functionals.

The more general result is:

$$\Psi 
ightarrow r^{eta} e^{-\sqrt{2E_I}r}.$$

Prove it and show that  $\beta = -1 + 1/\alpha$  where  $\alpha = \sqrt{2E_I}$ .

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## Electron–Nuclear cusp condition I

$$\left. \frac{\partial \Psi}{\partial r_{i\alpha}} \right|_{r_{i\alpha}=0} = -Z_{\alpha} \Psi(r_{i\alpha}=0)$$

We will prove the electron–electron cusp condition later, when discussing basis sets.

# Electron–Nuclear cusp condition II

Consider a 1-electron system (that's all we need for this cusp condition) with a nucleus of charge Z at the origin:

$$\hat{\mathcal{H}} = -\frac{1}{2}\nabla^2 + V(\mathbf{r})$$

$$= -\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\hat{l}^2}{r^2}\right) - \frac{Z}{r}.$$
(15)
(16)

If  $\hat{H}\Psi = E\Psi$ , where E is a finite, bound-state energy, then we can define the local energy function:

$$E\Psi = \hat{H}\Psi$$
$$= -\frac{1}{2}\frac{\partial^2\Psi}{\partial r^2}$$
$$-\frac{1}{r}\frac{\partial\Psi}{\partial r} - \frac{\hat{f}^2\Psi}{r^2} - \frac{Z}{r}\Psi.$$

### Electron–Nuclear cusp condition III

Now, since the energy *E* is finite, the L.H.S. is finite everywhere, and therefore the R.H.S. must also remain finite for all *r*. In fact, it must be a constant for all *r*! But the R.H.S. contains three terms that diverge as  $r \rightarrow 0$ , i.e., as the electron approaches the nucleus. The only way for the R.H.S. to remain finite is for these three terms to cancel as  $r \rightarrow 0$ .

The  $\hat{l}^2 \Psi$  term vanishes for all spherical states, and can be made to vanish for more general states by taking the spherical average about the nuclear position.

How do we see this? Q: Hint:  $\hat{I}^2 \Psi$  can be expanded in terms of spherical harmonics and radial functions. What is the spherical average of  $Y_{lm}$  for I > 0?

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### Electron–Nuclear cusp condition IV

The other two terms must cancel giving:

$$0 = -\frac{2}{r}\frac{\partial\Psi}{\partial r} - \frac{Z}{r}\Psi$$

and since  $\Psi(0) \neq 0$ , we have

$$\left.\frac{\partial\Psi}{\partial r}\right|_{r=0}=-Z\Psi(0).$$

Or, more generally,

$$\left\langle \frac{\partial \Psi}{\partial r} \right\rangle_{\rm sph} \bigg|_{r=0} = -Z \langle \Psi(0) \rangle_{\rm sph}$$

## Electron–Nuclear cusp condition V

The e-e cusp condition proofs are more involved. Here we will look at a simplified 'proof' of the condition.

Consider two electrons *i* and *j* approaching each other. We will work in the limit  $r \equiv r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \rightarrow 0$ . Here, the only interactions that matter are those involving these two electrons. Hence the effective 2-particle Schrödinger equation can be written as follows:

$$E\Psi = \left(-rac{1}{2\mu}
abla^2 + rac{1}{r}
ight)\Psi,$$

where the reduced mass is  $\mu = 1/2$  (Why?). Now let's use the same ideas we used for the electron-nuclear cusp. For the system in a spherically symmetric state (this requires that the electron

## Electron–Nuclear cusp condition VI

spins are opposite, i.e. we have a singlet state. A triplet state would have a node at  $r_{ij} = 0$ ) we can write

$$\begin{aligned} \Xi \Psi &= \hat{H} \Psi \\ &= -\frac{\partial^2 \Psi}{\partial r^2} \\ &- \frac{2}{r} \frac{\partial \Psi}{\partial r} - \frac{\hat{I}^2 \Psi}{2r^2} + \frac{1}{r} \Psi. \end{aligned}$$

Since the L.H.S. is finite, the divergent terms on the R.H.S. need to cancel. For a spherically symmetric state,  $\hat{I}^2 \Psi = 0$ , so we must have, at electron coalscence

$$-\frac{2}{r}\frac{\partial\Psi}{\partial r}+\frac{1}{r}\Psi=0$$

### Electron–Nuclear cusp condition VII

or, remembering that r is short for  $r_{ij}$ ,

$$\left.\frac{\partial\Psi}{\partial r_{ij}}\right|_{r_{ij}=0}=+\frac{1}{2}\Psi(r_{ij}=0).$$

This holds for the singlet state only! For the triplet state instead of a half, we get a +1/4 (no proof). There are cusp conditions involving more than two electrons. Or indeed, the conditions could involve two electrons and a nucleus, and another other number and permutation of particles.

### Variational Principle I

Variational stability For all possible variations  $\delta \Psi$ , s.t.,  $\langle \delta \Psi | \Psi \rangle = 0$  (i.e., the variations are orthogonal to  $\Psi$ ),  $\langle \delta \Psi | \hat{H} | \Psi \rangle = E \langle \delta \Psi | \Psi \rangle = 0$ ,

i.e.,  $\Psi$  is stable to these variations to first order.

Variational Principle II

Let the exact (ground state) eigenvalue equation be

 $\hat{H}|0\rangle = E_0|0\rangle.$ 

Let  $|\tilde{0}\rangle$  be an approximation to  $|0\rangle$  and let

$$|\tilde{0}
angle = |0
angle + |\delta
angle$$

where  $|\delta\rangle$  is an allowed variation. We will often impose intermediate normalisation (this is a convenient way of ensuring normalization to first order in the variation) and require that  $\langle 0|\delta\rangle = 0$ , but we will not do this here.

Hückel Theory

### Variational Principle III

$$\begin{split} E[0+\delta] &= \frac{\langle 0+\delta|H|0+\delta\rangle}{\langle 0+\delta|0+\delta\rangle} \\ &= \frac{\langle 0|H|0\rangle + \langle 0|H|\delta\rangle + \langle \delta|H|0\rangle + \langle \delta|H|\delta\rangle}{\langle 0|0\rangle + \langle 0|\delta\rangle + \langle \delta|0\rangle + \langle \delta|\delta\rangle} \\ &= \left(E_0 + \langle 0|H|\delta\rangle + \langle \delta|H|0\rangle + \mathcal{O}(\delta^2)\right) \\ &\times \left(1 - \left(\langle 0|\delta\rangle + \langle \delta|0\rangle\right) + \mathcal{O}(\delta^2)\right) \\ &= E_0 + \langle 0|H - E_0|\delta\rangle + \langle \delta|H - E_0|0\rangle + \mathcal{O}(\delta^2) \\ &= E_0 + \delta E + \mathcal{O}(\delta^2) \end{split}$$

Now  $\delta E = 0$  whenever  $\hat{H}|0\rangle = E_0|0\rangle$ , therefore the state  $|0\rangle$  is a stationary state point in the energy functional  $E[\tilde{0}]$ .

### Variational Principle IV

Conversely, we will now show that all stationary states of  $E[\tilde{0}]$  are eigenstates of  $\hat{H}$ . Notice that here we are treating  $E[\tilde{0}]$  as a *functional* of  $\tilde{0}$ .

Let  $|0\rangle$  be a stationary point (state) of  $E[\tilde{0}]$ . By definition, for the variation  $|\delta\rangle$  in  $|0\rangle$ , all terms in  $E[0 + \delta]$  that linear in  $|\delta\rangle$  must vanish. From the previous page his means that  $\delta E = 0$ , or

$$\delta E = 0 = \langle 0|H - E[0]|\delta \rangle + \langle \delta|H - E[0]|0 \rangle.$$

Now consider the variation  $i|\delta\rangle$ . This gives us the condition

$$\delta E = 0 = \langle 0|H - E[0]|\delta\rangle - \langle \delta|H - E[0]|0\rangle.$$

Therefore, adding them up we get

$$\mathsf{0} = \langle \delta | \mathsf{H} - \mathsf{E}[\mathsf{0}] | \mathsf{0} 
angle \quad orall \quad |\delta 
angle.$$

Variational Principle V

Since this must hold for all variations  $|\delta\rangle$ , we must have

$$\hat{H}|0
angle\equiv E[0]|0
angle\equiv E_{0}|0
angle,$$

i.e.,  $|0\rangle$  is an eigenstate of  $\hat{H}$ .

Hence the variational principle states that the solution of  $\hat{H}|0\rangle = E_0|0\rangle$  is equivalent to a variational optimization of E[0].

# The Hellmann–Feynmann Theorem I

For a stationary state, the first-order change in the energy due to a perturbation may be calculated as the expectation value of the perturbation operator:

$$\frac{\partial E(\alpha)}{\partial \alpha}\Big|_{\alpha=0} = \langle \Psi | V | \Psi \rangle.$$

Proof:

Let  $H(\alpha) = H + \alpha V$  where V is the perturbation. Further, let  $|\Psi_{\alpha}\rangle$  be a stationary state of  $H(\alpha)$ , i.e.,

$$H(\alpha)|\Psi_{\alpha}\rangle = E(\alpha)|\Psi_{\alpha}\rangle.$$

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## The Hellmann–Feynmann Theorem II

This implies

$${\sf E}(lpha)=rac{\langle \Psi_lpha|{\cal H}(lpha)|\Psi_lpha
angle}{\langle \Psi_lpha|\Psi_lpha
angle}$$

Therefore, using the definition  $|\Psi\rangle=\left.|\Psi_{\alpha}\rangle\right|_{\alpha=0}$ , and  $\left.\langle\Psi_{\alpha}|\Psi_{\alpha}\rangle=1$ ,

$$\begin{aligned} \frac{\partial E(\alpha)}{\partial \alpha} \Big|_{\alpha=0} &= \left. \frac{\partial}{\partial \alpha} \frac{\langle \Psi_{\alpha} | H(\alpha) | \Psi_{\alpha} \rangle}{\langle \Psi_{\alpha} | \Psi_{\alpha} \rangle} \right|_{\alpha=0} \\ &= 2 \Re \langle \left. \frac{\partial \Psi_{\alpha}}{\partial \alpha} \right|_{\alpha=0} | H - E(0) | \Psi \rangle + \langle \Psi | V | \Psi \rangle \end{aligned}$$

and since  $H(0)|\Psi
angle=E(0)|\Psi
angle$ , we get

$$\frac{\partial E(\alpha)}{\partial \alpha}\Big|_{\alpha=0} = \langle \Psi | V | \Psi \rangle.$$

# The Hellmann–Feynmann Theorem III

This theorem is useful for evaluating properties and in geometry optimizations. For example, in the presence of an electric field F along x, the Hamiltonian is H(F) = H - Fx. From the Hellmann–Feynmann theorem we can evaluate the dipole moment  $\mu_x$  as

$$\mu_{\mathsf{x}} = \left. \frac{\partial \mathsf{E}}{\partial \mathsf{F}} \right|_{\mathsf{F}=0} = \langle \Psi | \mathsf{x} | \Psi \rangle.$$

To see how it can be used to determine the force on a nucleus consider the Hamiltonian with nuclei at  $R_I$  displaced by  $\alpha_I$ :  $H(R_I + \alpha_I)$ . Let  $|\Psi\rangle$  be the eigenfunction of  $H(R_I)$ , i.e., at  $\alpha_I = 0$ .

## The Hellmann–Feynmann Theorem IV

We can write

$$H(R_{I} + \alpha_{I}) = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} + \sum_{j > i} \frac{1}{|r_{i} - r_{j}|}$$
  
$$- \sum_{il} \frac{Z_{I}}{|r_{i} - R_{I} - \alpha_{I}|}$$
  
$$+ \sum_{J > I} \frac{Z_{I}Z_{J}}{|R_{I} + \alpha_{I} - R_{J} - \alpha_{J}|}$$
  
$$= H(R_{I}) - \sum_{il} \frac{Z_{I}(r_{i} - R_{I}) \cdot \alpha_{I}}{|r_{i} - R_{I}|^{3}}$$
  
$$- \sum_{J > I} \frac{Z_{I}Z_{J}(R_{I} - R_{J}) \cdot \alpha_{I}}{|R_{I} - R_{J}|^{3}} + \mathcal{O}(\alpha^{2})$$

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# The Hellmann–Feynmann Theorem V

We have used the expansion in the last step as we know we need to differentiate w.r.t.  $\alpha_I$  and then set  $\alpha_I = 0$ . I.e., we have written the Hamiltonian in the form  $H(R_I + \alpha_I) = H(R_I) + \alpha_I \cdot V$ , with

$$V = -\sum_{il} \frac{Z_l(r_i - R_l)}{|r_i - R_l|^3} - \sum_{J>l} \frac{Z_l Z_J(R_l - R_J)}{|R_l - R_J|^3}$$

Hence, from the H-F theorem,

$$\frac{\partial E}{\partial \alpha_I}\Big|_{\alpha_I=0} = -\langle \Psi | \sum_{iI} \frac{Z_I(r_i - R_I)}{|r_i - R_I|^3} | \Psi \rangle$$
$$- \sum_{J>I} \frac{Z_I Z_J(R_I - R_J)}{|R_I - R_J|^3}$$

This makes it easy to evaluate first derivatives of the energy w.r.t. nuclear coordinates. So we can do geometry optimizations.

# The Hellmann–Feynmann Theorem VI

This theorem holds not only for the exact wavefunction but also Q: for variationally optimized wavefunctions such as  $|\mathbf{c}\rangle$ . Prove this.

**Pulay Forces**: We usually obtain variational wavefunctions using nuclear-centered basis sets. In this case, the basis space alters with changes in the nuclear positions. So there are terms in the gradient w.r.t. the basis functions. These terms are called Pulay forces after Peter Pulay.

You will have come across the Virial theorem in the form:

$$\langle V \rangle = -2 \langle T \rangle,$$

that is, the expectation value of a Coulomb potential  $\hat{V}$  is twice the expectation value of the kinetic energy operator  $\hat{T}$ . The molecular virial theorem takes the form

$$2\langle T \rangle + \langle V(R) \rangle + \langle \frac{\partial V(\alpha R)}{\partial \alpha} \Big|_{\alpha=1} \rangle = 0.$$

This may seem rather strange, but, as we shall see, the additional term is a consequence of the Born–Oppenhiemer approximation.

To prove the molecular virial theory we will use the idea of uniform scaling (we will also use this idea a lot when we take up density functional theory):

#### Theorem

Under uniform scaling of the electronic coordinates:

$$r_i o lpha r_i,$$
  
 $\psi(r_i) o \psi_{lpha}(r_i) = lpha^{3N/2} \psi(lpha r_i).$ 

This form of the scaling is needed to ensure normalization.

Q: Prove that as defined above,  $\psi_{\alpha}$  is normalized.

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We need two more identities:

• 
$$\langle \psi_{\alpha} | T | \psi_{\alpha} \rangle = \alpha^2 \langle \psi | T | \psi \rangle$$
  
•  $\langle \psi_{\alpha} | V(R) | \psi_{\alpha} \rangle = \alpha \langle \psi | V(\alpha R) | \psi \rangle$ 

## The Virial Theorem IV

Proof of the first result:

$$\begin{split} \psi_{\alpha}|T|\psi_{\alpha}\rangle &= \alpha^{3N} \int \psi^{*}(\alpha r_{i}) \left(-\frac{1}{2} \sum_{i} \nabla_{i}^{2}\right) \psi(\alpha r_{i}) \prod_{i} \mathrm{d}r_{i} \\ &= \int \psi^{*}(\alpha r_{i}) \left(-\frac{1}{2} \alpha^{2} \sum_{i} \nabla^{\alpha}_{i}^{2}\right) \psi(\alpha r_{i}) \prod_{i} \mathrm{d}(\alpha r_{i}) \\ &= \alpha^{2} \int \psi^{*}(r_{i}') \left(-\frac{1}{2} \sum_{i} \nabla^{\prime}_{i}^{2}\right) \psi(r_{i}') \prod_{i} \mathrm{d}(r_{i}') \\ &= \alpha^{2} \langle \psi|T|\psi \rangle \end{split}$$

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### The Virial Theorem V

Now consider

$$\begin{split} \frac{\partial E(\alpha)}{\partial \alpha} \Big|_{\alpha=1} &= \left. \frac{\partial}{\partial \alpha} \langle \psi_{\alpha} | H(R) | \psi_{\alpha} \rangle \right|_{\alpha=1} \\ &= \left. \frac{\partial}{\partial \alpha} \left( \alpha^{2} \langle \psi_{\alpha} | T | \psi_{\alpha} \rangle + \alpha \langle \psi_{\alpha} | V(\alpha R) | \psi_{\alpha} \rangle \right) \right|_{\alpha=1} \\ &= \left. 2\alpha \langle \psi | T | \psi \rangle + \langle \psi | V(\alpha R) | \psi \rangle + \alpha \langle \psi | \frac{\partial V(\alpha R)}{\partial \alpha} | \psi \rangle \right|_{\alpha=1} \end{split}$$

Therefore we get the molecular virial theorem:

$$2\langle\psi|T|\psi
angle+\langle\psi|V(R)|\psi
angle=-\langle\psi|rac{\partial V(lpha R)}{\partiallpha}igg|_{lpha=1}|\psi
angle$$

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For exact or variational states, using the Hellmann–Feynmann theorem we know that

$$\frac{\partial E(\alpha R)}{\partial \alpha}\Big|_{\alpha=1} = \langle \psi | \frac{\partial V(\alpha R)}{\partial \alpha} \Big|_{\alpha=1} |\psi\rangle$$

so, the virial theorem becomes

$$2\langle\psi|T|\psi
angle+\langle\psi|V(R)|\psi
angle=-rac{\partial E(lpha R)}{\partiallpha}\Big|_{lpha=1}$$

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### The Virial Theorem VII

The R.H.S. is just the classical force w.r.t. uniform scaling of the nuclear framework.

This force vanishes at molecular equilibrium, at which point the molecular virial theorem becomes the more famaliar:

$$\langle \psi | T | \psi \rangle = -\frac{1}{2} \langle \psi | V(R_e) | \psi \rangle$$

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with all quantities evaluated at  $R = R_e$ .

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## Approximate Methods I

What are the methods we have to solve the Schrödinger equation for many electron systems?

- Variational principle
- Perturbation theory
- Non-perturbative, approximate methods

We will look at the first two now. You have already seen these before, but let's go over these again. The non-perturbative methods will be covered later in the course.

#### The Variational Method

We now apply the variational principle to a trial state  $|\mathbf{c}\rangle$  which contains a finite number of numerical parameters  $\mathbf{c}.$  Define

$$\Xi(\mathbf{c}) = rac{\langle \mathbf{c} | \mathcal{H} | \mathbf{c} 
angle}{\langle \mathbf{c} | \mathbf{c} 
angle}$$

The stationary points of  $E(\mathbf{c})$  will be approximate eigenstates of  $\hat{H}$ .

If the error in  $|0\rangle$  is  $|\delta\rangle$ , the error in  $E_0$  is only  $\mathcal{O}(\delta^2)$ , i.e., the energy is accurate to second-order in the error in the wavefunction.

Hückel Theory

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# The Variational Method II

#### Linear Expansions

$$|\mathbf{C}
angle = \sum_{i=1}^{M} c_i |i
angle$$

where  $|i\rangle$  will, in general, be an *N*-electron antisymmetric function (usually a Slater determinant).

$${m {f E}}({f c})=rac{\langle {f c}|{f H}|{f c}
angle}{\langle {f c}|{f c}
angle}$$

Define the electronic gradient:

$$E_i^{(1)}(\mathbf{c}) = \frac{\partial E(\mathbf{c})}{\partial c_i},$$

Hückel Theory

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## The Variational Method III

and the electronic Hessian:

$$E_{ij}^{(2)}(\mathbf{c}) = \frac{\partial^2 E(\mathbf{c})}{\partial c_i c_j}.$$

We need both quantities to determine and characterise the extrema of  $E(\mathbf{c})$ .

To evaluate these quantities write the energy function as

$$E(\mathbf{c})\langle \mathbf{c}|\mathbf{c}\rangle = \langle \mathbf{c}|H|\mathbf{c}\rangle,$$

Hückel Theory

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### The Variational Method IV

and differentiate w.r.t.  $c_i$  to get

$$\begin{split} E_i^{(1)}(\mathbf{c}) &= \frac{2\left(\langle i|H|\mathbf{c}\rangle - E(\mathbf{c})\langle i|\mathbf{c}\rangle\right)}{\langle \mathbf{c}|\mathbf{c}\rangle}\\ E_{ij}^{(2)}(\mathbf{c}) &= \frac{2\left(\langle i|H|j\rangle - E(\mathbf{c})\langle i|j\rangle\right)}{\langle \mathbf{c}|\mathbf{c}\rangle}\\ &- 2E_i^{(1)}(\mathbf{c})\frac{\langle j|\mathbf{c}\rangle}{\langle \mathbf{c}|\mathbf{c}\rangle} - 2E_j^{(1)}(\mathbf{c})\frac{\langle i|\mathbf{c}\rangle}{\langle \mathbf{c}|\mathbf{c}\rangle} \end{split}$$

At a stationary point,  $E_i^{(1)}(\mathbf{c}) = 0$ , therefore

$$\langle i|H|\mathbf{c}\rangle = E(\mathbf{c})\langle i|\mathbf{c}\rangle$$

# The Variational Method V

If we define the Hamiltonian and Overlap matrix elements:

$$egin{aligned} H_{ij} &= \langle i | H | j 
angle \ S_{ij} &= \langle i | j 
angle \end{aligned}$$

we get

Hc = E(c)Sc

This is a set of linear equations we need to solve to get the optimized states  $|\mathbf{C}\rangle$  and energies  $E(\mathbf{c})$ . If the basis states  $|i\rangle$  are orthonormal, i.e., if  $S_{ij} = \delta_{ij}$ , then the equations become

 $\mathbf{H}\mathbf{c} = E(\mathbf{c})\mathbf{c}.$ 

These equations have non-trivial solutions when

det  $|\mathbf{H} - F(\mathbf{c})\mathbf{S}| = 0^{-\langle \mathbf{c} \rangle \cdot \langle \mathbf{B} \rangle \cdot \langle \mathbf{B} \rangle \cdot \langle \mathbf{B} \rangle}$ 

The Variational Method VI

Since  $\hat{H}$  is Hermitian we have exactly M orthonormal solutions:

$$\mathbf{c}_{K}=\left(c_{1K},c_{2K},\cdots,c_{MK}\right)^{T}$$

s.t.  $\mathbf{c}_{K}^{T}\mathbf{c}_{L} = \delta_{KL}$  and

$$E_{\mathcal{K}} = E(\mathbf{c}_{\mathcal{K}}), \quad E_1 \leq E_2 \leq \cdots \leq E_{\mathcal{M}}.$$

The approximate wavefunctions are

$$|K
angle = \sum_{i=1}^{M} c_{iK} |i
angle.$$

### The Variational Method VII

We now need to characterise these stationary points using the electric Hessian. At the stationary point  $\mathbf{c}_{\mathcal{K}}$ ,  $E_i^{(1)}(\mathbf{c}_{\mathcal{K}}) = 0$ . Therefore, from the expression for the Hessian,

$$E_{ij}^{(2)}(\mathbf{c}_{\mathcal{K}}) = 2\left(\langle i|H|j\rangle - E(\mathbf{c}_{\mathcal{K}})\langle i|j\rangle\right).$$

This is the Hessian in terms of the  $|i\rangle$  basis set. We can express it in terms of the  $|K\rangle$  basis of eigenvectors using  $\sum_{i} \sum_{i} c_{iM} c_{jN}$  to get

$$E_{MN}^{(2)}(\mathbf{c}_{K}) = 2\left(\langle M|H|N\rangle - E(\mathbf{c}_{K})\langle M|N\rangle\right)$$
$$= 2(E_{M} - E_{K})\delta_{MN}.$$

Therefore, the eigenvalues of the Hessian at the stationary points are given by

$$E_{MM}^{(2)}(\mathbf{c}_K) = 2(E_M - E_K).$$

## The Variational Method VIII

That is,  $E_{MM}^{(2)}(\mathbf{c}_{\kappa})$  is twice the transition energy between state  $|\kappa\rangle$  and state  $|M\rangle$ .

We can make a number of observations from this:

- $E_{MN}^{(2)}(\mathbf{c}_K)$  is a singular matrix since  $E_{KK}^{(2)}(\mathbf{c}_K) = 0$ .
- Eigenstate  $|K\rangle$  has K 1 negative eigenvalues (in the absence of degenaricies) as  $E_M < E_K$  for M < K.
- Therefore, for K = 1 there are 0 negative eigenvalues, hence this state,  $|1\rangle$ , is a minimum.
- K = 2 has one negative eigenvalue, therefore it is a first-order saddle point. Etc. for the other states.

## The Variational Method IX

# **Upper bounds and the Hylleras–Undheim theorem** Consider two orthonormal sets of *N*-electron basis functions: $S' = \{|I'\rangle\}$ and $S'' = \{|I''\rangle\}$ s.t. $S' \subset S''$ . We have the eigenvalue equations (assume the eigenvalues are sorted in ascending order):

$$\mathbf{H'c'_K} = E'_K \mathbf{c'_K}$$
  
 $\mathbf{H''c''_K} = E''_K \mathbf{c''_K}$ 

Since  $S' \subset S''$ , we can express the eigenfunctions  $\{|K'\rangle\}$  in terms of the  $\{|K''\rangle\}$ :

$$|K'\rangle = \sum_{L} a_{KL} |L''\rangle.$$

Q: Show that  $\langle K'|K'\rangle = 1$  implies  $\sum_L |a_{KL}|^2 = 1$ .

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Approximate Methods

Hückel Theory

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# The Variational Method X

Now consider  $E'_1$ :

$$\begin{split} E_1' &= \langle 1|H|1 \rangle \\ &= \sum_{KL} a_{1K}^* \langle K''|H|L'' \rangle a_{1L} \\ &= \sum_K |a_{1K}|^2 E_K'' \geq E_1'' \sum_K |a_{1K}|^2 = E_1''. \end{split}$$

Therefore  $E_1'' \leq E_1'$ . I.e., in a linear variation method, the lowest eigenvalue will drop (or remain the same) as the variational space is increased.

This result is a special case of

Approximate Methods

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# The Variational Method XI

### Theorem

**Cauchy's Interval Theorem**: If  $S' \subset S''$ ,

$$E_{K}'' \leq E_{K}' \leq E_{K+\delta}'',$$

where  $\delta = \dim S'' - \dim S'$  is the difference in the dimensions of the two linear spaces.

For  $\delta = 1$  we get the Hylleras–Undheim Theorem.

# Raleigh–Schrödinger Perturbation Theory I

We will now briefly recap of Raleigh–Schrödinger perturbation theory. We use perturbation theory when we cannot solve a differential (or any other) equation exactly, but can find solutions to the major part of it; we then treat the remainder as a perturbation over the solution we can find. This is how it works:

• Split the Hamiltonian into two parts:

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{V}$$

where  $\mathcal{H}_0$  is a Hamiltonian which we know how to solve and  $\mathcal{V}$  contains that troublesome parts. We expect  $\mathcal{V}$  to be a perturbation so it must be small in some sense.

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# Raleigh–Schrödinger Perturbation Theory II

- $\lambda$  is a complex number that will be 1 for the physical solution. Think of the problem like this: We start from  $\lambda = 0$ . This gives the solution we already know. Then consider small, but non-zero  $\lambda$ ; develop a perturbation expansion; and then consider the limit  $\lambda \rightarrow 1$  and hope that our expansion is still meaningful (or convergent) in this limit.
- Let the solutions of  $\mathcal{H}_0$  be:

$${\cal H}_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)}$$

Here the '0' indicates that these eigenvalues and eigenfunctions are of *zeroth*-order in the perturbation  $\mathcal{V}$ . We will use the short-form:

$$|\Psi_i^{(0)}\rangle \equiv |i\rangle$$

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## Raleigh–Schrödinger Perturbation Theory III

• Express the solutions of  ${\mathcal H}$  in a power-series:

$$\Psi_{i} = \Psi_{i}^{(0)} + \lambda \Psi_{i}^{(1)} + \lambda^{2} \Psi_{i}^{(2)} + \dots = \sum_{n} \lambda^{n} \Psi_{i}^{(n)}$$
$$E_{i} = E_{i}^{(0)} + \lambda E_{i}^{(1)} + \lambda^{2} E_{i}^{(2)} + \dots = \sum_{n} \lambda^{n} E_{i}^{(n)}$$

• Energies can be calculated by collecting terms at various orders:

$$E_i^{(0)} = \langle \Psi_i^{(0)} | \mathcal{H}_0 | \Psi_i^{(0)} \rangle = \langle i | \mathcal{H}_0 | i \rangle$$
  

$$E_i^{(1)} = \langle \Psi_i^{(0)} | \mathcal{V} | \Psi_i^{(0)} \rangle = \langle i | \mathcal{V} | i \rangle$$
  

$$E_i^{(2)} = \langle \Psi_i^{(0)} | \mathcal{V} | \Psi_i^{(1)} \rangle$$

## Raleigh–Schrödinger Perturbation Theory IV

etc. for higher order terms.

• The first-order correction to the wavefunction is given by

$$|\Psi_{i}^{(1)}
angle = \sum_{n \neq 0} \frac{|n
angle \langle n|\mathcal{V}|i
angle}{E_{i}^{(0)} - E_{n}^{(0)}}$$

• So we get for the second-order energy correction:

$$E_i^{(2)} = \sum_{n \neq 0} \frac{|\langle n | \mathcal{V} | i \rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

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# Raleigh–Schrödinger Perturbation Theory V

Higher-order corrections to the wavefunction and the energy can be obtained by keeping more and more terms in the expansion. We often use these, but we must not assume that they will be meaningful. The problem here is that we cannot guarantee the convergence of perturbation expansions. These expansions are often divergent (bad!) or only asymtotically convergent (usuable with care!).

#### Wigner's 2n + 1 rule:

Q: This theorem states that a knowledge of the wavefunction to order n is sufficient to determine the energy to order 2n + 1. Show this.

### Calculations without a computer

When dealing with unsaturated conjugated systems (polyenes, acenes, graphene) we can use the Hückel approximation to allow us to perform calculations by hand (or a small computer). This method relies on the idea of  $\sigma - \pi$  separability: for a planar acene, the  $\pi$  orbitals (the  $p_z$ ) are of a different symmetry from the more tightly bound  $\sigma$  orbitals. The  $\sigma$  orbitals are symmetric under reflection in the plane of the molecule while the  $\pi$  orbitals change sign. Hence they do not mix. Consequently we can consider the  $\pi$  orbitals separately from the  $\sigma$ . In periodic systems this method goes by the name *tight binding*.

We start with the linear variation equations:

$$Hc = E(c)Sc$$

and assume that our basis space is orthonormal, i.e.,  $\boldsymbol{S}=\boldsymbol{I}.$  This gives

$$(\mathbf{H} - E\mathbf{I})\,\mathbf{c} = 0.$$

This has nontrivial solutions only if

$$\det |\mathbf{H} - E\mathbf{I}| = 0$$

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Now assume a very local form of  $\mathbf{H}$ :

$$H_{ij} = \begin{cases} \alpha & \text{if } i = j \\ \beta & \text{if } i \text{ and } j \text{ neighbours} \\ 0 & \text{otherwise.} \end{cases}$$

Here  $\alpha = \langle \pi_i | H | \pi_i \rangle$  can be regarded as the energy of the  $\pi_i$  orbital and  $\beta = \langle \pi_i | H | \pi_j \rangle$  (*i* and *j* are neighbouring atoms) can be regarded as a *resonance* integral coupling the two  $\pi$  orbitals.

How can we justify making all resonance integrals the same?You may think that there should be a dependence on the na-Q: ture of the C—C bond, i.e., whether it is a single, double or triple bond. The key here is that this approximation is valid for *delocalised* systems in which all C—C bonds are equivalent.

The idea here is that we solve for the energies  $\epsilon_i$  and calculate the total  $(\pi)$  energy of the system as

$$E_{\rm tot} = \sum_i \epsilon_i.$$

Here we have used the conventional notation  $\epsilon_i$  for the energies of the eigenstates.

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### Consider ethylene:

 $\mathbf{H} - \mathbf{C} = \mathbf{C} - \mathbf{H}$ 

we don't care about hydrogen atoms in the Hückel approximation so this becomes:

-----C = ------ CIt has only two carbon atoms so our basis set consists of two  $2p_{\pi}$  atomic orbitals. Call these  $\phi_1$  on carbon 1 and  $\phi_2$  on carbon 2. Therefore, the eigenstates will be of the form:

$$\psi_i = c_{1i}\phi_1 + c_{2i}\phi_2.$$

Using the Hückel rules we can write the Hamiltonian matrix as:

$$H_{i,j} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

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The secular equation is

$$\det \begin{vmatrix} \alpha - \epsilon & \beta \\ \beta & \alpha - \epsilon \end{vmatrix} = 0$$

which leads to

$$(\alpha - \epsilon)^2 - \beta^2 = 0$$

leading to the roots:

$$\epsilon_1 = \alpha + \beta$$
$$\epsilon_2 = \alpha - \beta$$

Substitute these energies in turn back into

 $(\mathbf{H} - E\mathbf{I})\mathbf{c} = 0.$ 

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which takes the form

$$c_{1i}(\alpha - \epsilon_i) + c_{2i}\beta = 0$$

to get

• For 
$$\epsilon_1$$
:  $c_{11} = c_{12} = c$  and  $\psi_1 = c(\phi_1 + \phi_2)$ .

• For  $\epsilon_2$ :  $c_{11} = -c_{12}$  and  $\psi_2 = c(\phi_1 - \phi_2)$ .

Since we have assumed the  $\phi_i$  are orthonormal, the normalization constant  $c = 1/\sqrt{2}$ .

Note that since both  $\alpha$  and  $\beta$  are negative,  $\epsilon_1 < \epsilon_2$ . We have solved our first many electron system by hand!

#### Now what about butadiene:

 $\frac{1}{1} C = C C = C C$  Show that the secular equation is

$$\det \begin{vmatrix} \alpha - \epsilon & \beta & 0 & 0\\ \beta & \alpha - \epsilon & \beta & 0\\ 0 & \beta & \alpha - \epsilon & \beta\\ 0 & 0 & \beta & \alpha - \epsilon \end{vmatrix} = 0$$

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and solve for the energies and eigenfunctions.