Exact Results, the Variational Principle and Hückel Theory

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Asymptotic form of $|\Psi\rangle$ |

Proof of the asymptotic form of the density/wavefunction:

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

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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

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

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

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

$$-\frac{1}{2}\frac{\partial^2}{\partial r^2}\psi(r) = E\psi(r). \tag{3}$$

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

$$\psi(r) \to c e^{-\sqrt{-2E}r}.$$
 (4)

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:

$$\hat{H}\Psi_N(1,2,...,N) = E_N\Psi_N(1,2,...,N)$$
(5)

As we pull one electron out, Ψ_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 Ψ_N .

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

$$\hat{H} = \hat{H}_{N-1} + \hat{H}_1. \tag{6}$$

Asymptotic form of $|\Psi\rangle$ V

Therefore

$$E_{N}\Psi_{N} = \hat{H}\Psi_{N} = (\hat{H}_{N-1} + \hat{H}_{1})\Psi_{N-1}\phi(r)$$
(7)
= $E_{N-1}\Psi_{N-1}\phi(r) + \Psi_{N-1}(\hat{H}_{1}\phi(r)).$ (8)

And so

$$\Psi_{N-1}(\hat{H}_1\phi(r)) = (E_N - E_{N-1})\Psi_{N-1}\phi(r).$$
(9)

On integrating out Ψ_{N-1} we get the 1-electron eigenvalue problem:

$$\hat{H}_1\phi(r) = (E_N - E_{N-1})\phi(r).$$
 (10)

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Q:

Asymptotic form of $|\Psi\rangle$ VI

Using the result for the 1-electron case (Eq. (4)) we get

$$\phi(r) \to e^{-\sqrt{-2(E_N - E_{N-1})}r}$$
(11)
$$\to e^{-\sqrt{2E_I}r},$$
(12)

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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Variational Principle I

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.

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Variational Principle 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).

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

If we define the Hamiltonian and Overlap matrix elements:

$$H_{ij} = \langle i|H|j\rangle$$
$$S_{ij} = \langle i|j\rangle$$

we get

Variational Principle III

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

 $\det |\mathbf{H} - E(\mathbf{c})\mathbf{S}| = 0.$

Variational Principle IV

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

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

Variational Principle V

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 $\{|K''\rangle\}$:

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

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

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Variational Principle VI

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

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Variational Principle VII

Theorem

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

$$E_K'' \le E_K' \le E_{K+\delta}'',$$

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.

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.,

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

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 μ_x as

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

To see how it can be used to determine the force on a nucleus consider the Hamiltonian with nuclei at R_I displaced by α_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. α_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.

The Virial Theorem I

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.

The Virial Theorem II

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 elecronic 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, ψ_{α} is normalized.

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The Virial Theorem III

We need two more identities:

•
$$\langle \psi_{\alpha} | T | \psi_{\alpha} \rangle = \alpha^2 \langle \psi | T | \psi \rangle$$

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

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The Virial Theorem IV

Proof of the first result:

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

The Virial Theorem V

Now consider

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

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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The Virial Theorem VI

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

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

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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:

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

with all quantities evaluated at $R = R_e$.

Hückel Theory I

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 π orbitals (the p_z) are of a different symmetry from the more tightly bound σ orbitals. The σ orbitals are symmetric under reflection in the plane of the molecule while the π orbitals change sign. Hence they do not mix. Consequently we can consider the π orbitals separately from the σ . In periodic systems this method goes by the name *tight binding*.

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Hückel Theory II

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

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

Hückel Theory III

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 π_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 π 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.

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Hückel Theory IV

The idea here is that we solve for the energies ϵ_i and calculate the total (π) energy of the system as

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

Here we have used the conventional notation ϵ_i for the energies of the eigenstates.

Hückel Theory V

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 ϕ_1 on carbon 1 and ϕ_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:

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

Hückel Theory VI

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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Hückel Theory VII

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 ϕ_i are orthonormal, the normalization constant $c = 1/\sqrt{2}$.

Note that since both α and β are negative, $\epsilon_1 \langle \epsilon_2$.

We have solved our first many electron system by hand!

Hückel Theory VIII

Now what about butadiene:

 $\begin{array}{c} \hline C & = & C \\ \hline Show that the secular equation is \end{array}$

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

and solve for the energies and eigenfunctions.