Chapter 8 - The Variational Principle (for the energy)

In quantum mechanics there are variational principles for a wide variety of parameters: energy, log. derivative, tan (phase shift), scattering matrix ...

The basic idea: you have a decent guess at the wave function (usually called the trial wave function). There is a functional that gives the desired variable accurate to 2nd order in the difference of the trial function and the exact wave function.

The trial function will be written symbolically as

$\psi_{tr} = \psi_{ex} + \delta\psi$ (ψ_{ex} is the exact, but unknown, wave function)

The book shows $E_{gs} \leq \langle \psi_{tr} | H | \psi_{tr} \rangle$ assuming $\langle \psi_{tr} | \psi_{tr} \rangle = 1$

These notes will take a different perspective.

First do the case for the ground state.

$$E_{gs} = \frac{\langle \psi_{tr} | H | \psi_{tr} \rangle}{\langle \psi_{tr} | \psi_{tr} \rangle} + O(\delta\psi^2)$$

To show this, we only need the Hermiticity of H.
How to show? Plug ψ_{tr} into expression

$$\begin{aligned}\langle \psi_{tr} | H | \psi_{tr} \rangle &= \langle \psi_{ex} | H | \psi_{ex} \rangle + \langle \delta\psi | H | \psi_{ex} \rangle + \langle \psi_{ex} | \underset{\leftarrow}{H} | \delta\psi \rangle + \langle \delta\psi | H | \delta\psi \rangle \\ &= E_{gs} + E_{gs} \langle \delta\psi | \psi_{ex} \rangle \overset{\rightarrow}{+} E_{gs} \langle \psi_{ex} | \delta\psi \rangle + E_{gs} \langle \delta\psi | \delta\psi \rangle \\ &\qquad + \langle \delta\psi | H - E_{gs} | \delta\psi \rangle \\ &= E_{gs} \langle \psi_{tr} | \psi_{tr} \rangle + \langle \delta\psi | H - E_{gs} | \delta\psi \rangle\end{aligned}$$

Divide this by the normalization integral

$$\frac{\langle \psi_{tr} | H | \psi_{tr} \rangle}{\langle \psi_{tr} | \psi_{tr} \rangle} = E_{gs} + \frac{\langle \delta\psi | H - E_{gs} | \delta\psi \rangle}{\langle \psi_{tr} | \psi_{tr} \rangle} \qquad \text{q.e.d.}$$

Why is the last term positive?? The left hand side gives an <u>upper bound</u> on the ground state energy. You don't need to know $\delta\psi$

$E_{gs} \leq \langle \psi_{tr} | H | \psi_{tr} \rangle / \langle \psi_{tr} | \psi_{tr} \rangle$

Important: This treatment can be extended to any eigenstate

$$\psi_{n,tr} = \psi_n + \delta\psi_n$$

$$\frac{\langle \psi_{n,tr} | H | \psi_{n,tr} \rangle}{\langle \psi_{n,tr} | \psi_{n,tr} \rangle} = E_n + \frac{\langle \delta\psi_n | H - E_n | \delta\psi_n \rangle}{\langle \psi_{tr,n} | \psi_{tr,n} \rangle}$$

However, the last term on the right hand side can be positive or negative, unless!! $\delta\psi_n$ is orthogonal to all eigenstates with energy less than E_n.

Example: Use the trial wave function $\psi_{tr}(x) = A \cdot x \cdot (a-x)$ to estimate the ground state energy of the infinite square well.

Find A $\quad A^2 \int_0^a x^2 (a-x)^2 dx = A^2 \int_0^a a^2x^2 - 2ax^3 + x^4 dx = A^2 a^5 \left(\frac{1}{3} - \frac{2}{4} + \frac{1}{5}\right)$

$= A^2 a^5/30 \quad \Rightarrow \quad A = (30/a^5)^{1/2}$

Compute $\langle \psi_{tr} | H | \psi_{tr} \rangle = A^2 \int_0^a x(a-x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} x(a-x)\right) dx$

$= A^2 \int_0^a x(a-x) \frac{\hbar^2}{m} dx = A^2 \frac{\hbar^2}{m} \int_0^a xa - x^2 dx$

$= A^2 \frac{\hbar^2}{m} a^3 \left(\frac{1}{2} - \frac{1}{3}\right) = \frac{30}{a^5} \frac{\hbar^2}{m} a^3 \frac{1}{6} = \frac{5\hbar^2}{ma^2}$

Compare to exact grnd state $E_{gs} = \frac{\hbar^2 \pi^2}{2ma^2} = 4.935 \frac{\hbar^2}{ma^2}$

The variational princ. gave an energy too high by 1.3%

What trial function could use for 1st excited state of the infinite square well? $\psi_{tr,2} = A \cdot x \cdot (a-x) \cdot (x - a/2)$

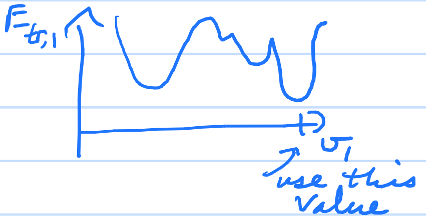
↑ node in middle

Why is this method called "variational principle"? In the trial function have variables that can change. Since the energy estimate has error quadratic in $\delta\psi$, change the variables until closest to exact E. How do you know when the energy estimate is closest?

$\Psi_{tr,n}(x, v_1, v_2, v_3 \ldots)$ a trial function with several variables $v_1, v_2 \ldots$

$$E_{tr,n}(v_1, v_2, v_3 \ldots) = \frac{\langle \Psi_{tr,n} | H | \Psi_{tr,n} \rangle}{\langle \Psi_{tr,n} | \Psi_{tr,n} \rangle}$$

For one variable looks like



why?

Method: 1) Find $v_1, v_2, \ldots v_m$ where $\frac{\partial E_{tr,n}}{\partial v_1} = 0$, $\frac{\partial E_{tr,n}}{\partial v_2} = 0$, ...

2) once you've found $v_1, v_2 \ldots$, substitute back into $E_{tr,n}$

See many examples in textbook.

Example with nonlinear variation: Griffiths Examples 8.1, 8.2 Sec 8.2, Sec 8.3

Example with nonlinear variation: In 1D, any potential with $V(x) \leq 0$ and $V(x \to \infty) = 0$ and $V(x \to -\infty) = 0$ has at least one bound state. Test on $V(x) = -V_0 e^{-ax^2}$

Use trial fct $\Psi_{tr} = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2}$

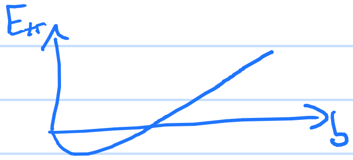
$$\langle \Psi_{tr} | \frac{P^2}{2m} | \Psi_{tr} \rangle = \frac{1}{2m} \langle P\Psi_{tr} | P\Psi_{tr} \rangle = \sqrt{\frac{2b}{\pi}} \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left(\frac{\partial e^{-bx^2}}{\partial x} \right)^2 dx$$

$$= \sqrt{\frac{2b}{\pi}} \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} 4b^2 x^2 e^{-bx^2} dx = \sqrt{\frac{2b}{\pi}} \frac{\hbar^2}{2m} 4b^2 \sqrt{\pi} \frac{1}{2(2b)^{3/2}} = \frac{\hbar^2 b}{2m}$$

$$\langle \Psi_{tr} | V | \Psi_{tr} \rangle = -V_0 \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} e^{-(2b+a)x^2} dx = -V_0 \sqrt{\frac{2b}{\pi}} \sqrt{\frac{\pi}{2b+a}} = -V_0 \sqrt{\frac{2b}{2b+a}}$$

Put together to get energy estimate

$$E_{tr,gs} = \frac{\hbar^2 b}{2m} - V_0 \sqrt{\frac{2b}{2b+a}}$$



Actual ground state energy is less than minimum $\Rightarrow E_{gs} < 0$
$\Rightarrow$ At least 1 bound state

For barely bound $a >> b$ $\quad E_{tr,gs} \cong \frac{\hbar^2 b}{2m} - \frac{V_0}{\sqrt{a}} \sqrt{2b}$

Use this expression to find b

$$\frac{\partial E_{tr}}{\partial b} = \frac{\hbar^2}{2m} - \frac{V_0}{\sqrt{a}\sqrt{2b}} = 0 \quad \Rightarrow \quad \sqrt{b} = \frac{V_0}{\sqrt{2a}}\frac{2m}{\hbar^2}$$

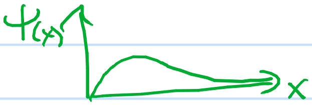
Substitute back into the expression for E_{tr}

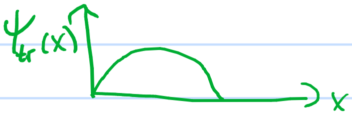
$$E_{tr} = \frac{\hbar^2}{2m}\frac{V_0^2}{2a}\frac{4m^2}{\hbar^4} - \frac{V_0\sqrt{2}}{\sqrt{a}}\frac{V_0}{\sqrt{2a}}\frac{2m}{\hbar^2} = \frac{2m}{\hbar^2}\frac{V_0^2}{2a} - \frac{2m}{\hbar^2}\frac{V_0^2}{a} = -\frac{2m}{\hbar^2}\frac{V_0^2}{2a}$$

The actual ground state energy is less than this

Another nonlinear variation example: Estimate the ground state energy for a constant negative force plus an infinite wall at $x=0$.

The wave function has to go to 0, linearly as $x \to 0$
" " " " " " as $x \to \infty$.





$$\psi_{tr}(x) = A\,x\,(a-x)$$

Use the info from the ∞ square well example $A = \sqrt{\frac{30}{a^5}}$

$$\langle \psi_{tr} | KE | \psi_{tr} \rangle = \frac{5\hbar^2}{ma^2}$$

$$\langle \psi_{tr} | V | \psi_{tr} \rangle = \frac{30}{a^5} F \int_0^a x^3 (a-x)^2 dx = \frac{30}{a^5} F \int_0^a x^3 a^2 - 2x^4 a + x^5 dx$$

$$= \frac{30}{a^5} F a^6 \left(\frac{1}{4} - \frac{2}{5} + \frac{1}{6}\right) = \frac{30}{a^5} F a^6 \frac{1}{60} = \frac{1}{2} F a$$

Combine $E_{tr} = \frac{5\hbar^2}{ma^2} + \frac{1}{2}Fa$

$$\frac{\partial E_{tr}}{\partial a} = 0 = -\frac{10\hbar^2}{ma^3} + \frac{F}{2} \Rightarrow a^3 = \frac{20\hbar^2}{Fm}$$

$$E_{tr} = \frac{5\hbar^2}{m}\left(\frac{Fm}{20\hbar^2}\right)^{2/3} + \frac{1}{2}F\left(\frac{20\hbar^2}{Fm}\right)^{1/3} = \left(\frac{F^2\hbar^2}{m}\right)^{1/3}\left[\frac{5}{(20)^{2/3}} + \frac{(20)^{1/3}}{2}\right]$$

$$= \left(\frac{F^2\hbar^2 20}{m}\right)^{1/3}\frac{3}{4}$$

Check units

The exact eigenenergies are $E_n = -\left(\frac{F^2\hbar^2}{2m}\right)^{1/3} a_n$ ← zeros of the Airy function

$-2.3381, -4.08795, \ldots$

$20^{1/3}\frac{3}{4} = 2.0358 > \frac{2.33811}{2^{1/3}} = 1.85576$ ($\simeq 10\%$ too high)

The vast majority of times when I've used the variational principle is with <u>linear</u> variables.

$$\Psi_{tr,n} = y_1(x)\, a_{1,n} + y_2(x)\, a_{2,n} + y_3(x)\, a_{3,n} + \cdots$$

Most common case $\int_{-\infty}^{\infty} y_n^*(x)\, y_m(x)\, dx = \delta_{nm}$

For simplicity only look at case where the y's are real and the Ψ_{tr} is real.

$$\langle \Psi_{tr,n} | H | \Psi_{tr,n} \rangle = \langle \Psi_{tr,n} | \Psi_{tr,n} \rangle E_{tr,n}$$

$$\sum_{m,m'} H_{m,m'}\, a_{m,n}\, a_{m',n} = \sum_{m} a_{m,n}\, a_{m,n}\, E_{tr,n}$$

Take the derivative of both sides with respect to $a_{m'',n}$ and remember $\partial E_{tr,n} / \partial a_{m'',n} = 0$

$$\sum_m H_{m,m''}\, a_{m,n} + \sum_m H_{m'',m}\, a_{m,n} = 2 \sum_m H_{m'',m}\, a_{m,n} = 2\, a_{m'',n}\, E_{tr,n}$$

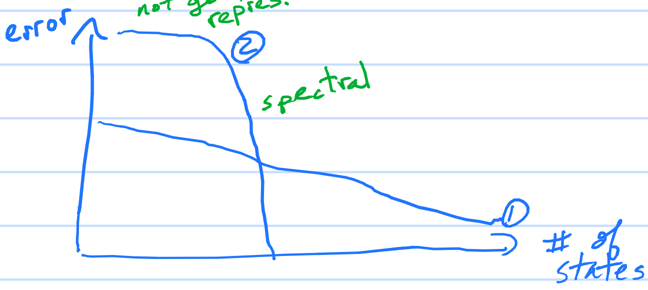
$$\underline{\underline{H}}\, \vec{a}_n = \vec{a}_n\, E_{tr,n}$$

The $E_{tr,n}$ are the <u>eigenvalues</u> of the matrix $\underline{\underline{H}}$ and the $\vec{a}$ are the <u>eigenvectors</u>.

Most typically The $E_{tr,n}$ with smaller n are the most accurate.

Two strategies are prevalent: 1) have the y_n be eigenstates of Hamiltonian similar to one you're trying to solve (most commonly used when computational resources are limited) or 2) choose y_n for ease of evaluating H_{nm} and just <u>hammer</u> the problem with a gojillian states

Convergence properties of two methods



Test case: use $\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$ to find the eigenstates and eigenvalues of $V(x) =$ 

$= \infty \quad x < 0$

$= Fx \quad x > 0$

$$H_{nn'} = KE_{n,n'} + V_{n,n'}$$

$$KE_{n,n'} = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \delta_{nn'}$$

$$V_{nn'} = F \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \sin\left(\frac{n'\pi x}{a}\right) x \, dx = 2aF \int_0^1 \sin(n\pi x) \sin(n'\pi x) \, x \, dx$$

$$= 2aF \frac{1}{4} \qquad n = n'$$

$$= 2aF \left\{ \left[\frac{1}{(n'+n)^2} - \frac{1}{(n'-n)^2} \right] / \pi^2 \right\} \frac{1-(-1)^{n'+n}}{2}$$ only nonzero $n'+n =$ odd

Need to choose a larger than the extent of the wave function or the infinite wall at a shifts the energy but if a is too big then need a lot of wave functions

$\hbar^2/ma^2$ and Fa are both energy scales $\Rightarrow a^3 \propto \frac{\hbar^2}{mF}$ $\quad a = C\left(\frac{\hbar^2}{mF}\right)^{1/3}$

The energy scale is $Fa = \mathcal{E}_{sc} = \left(\frac{\hbar^2 F^2}{m}\right)^{1/3}$

$$KE_{nn'} = \mathcal{E}_{sc} \frac{\pi^2 n^2}{2C^2} \delta_{nn'} \qquad V_{nn'} = \frac{1}{2} \mathcal{E}_{sc} C \delta_{nn'}$$

$$= 2\mathcal{E}_{sc} C \left\{ \left[\frac{1}{(n'+n)^2} - \frac{1}{(n'-n)^2} \right] / \pi^2 \right\} \frac{1-(-1)^{n+n'}}{2}$$

See plots and data for energies and wave functions

In much of atoms, molecules, ... The electronic states are determined using a mix of linear and non-linear variational parameters. As an extreme example, the non-relativistic, ∞ mass, point charge He ground state energy is known to 24 digits. This is much more accurate than the fundamental constants that go into the definition of the energy scale $\mathcal{E}_{sc} = e^2/4\pi\epsilon_0 a_0$

The following is the standard undergrad textbook derivation of the He ground state energy, but I compute the $1/r_{12}$ matrix element using a different idea.

The He Hamiltonian is $H = \frac{p_1^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$

$r_{12}^2 = r_1^2 + r_2^2 - 2\vec{r}_1\cdot\vec{r}_2$

The leading term in the two electron wave function is a spherically symmetric wave function for each individual electron. If the last term in the Hamiltonian is removed, then this is exact.

$$\psi_{tr} = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr_1/a_0} \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr_2/a_0} = \psi_{100}(r_1;Z)\,\psi_{100}(r_2;Z)$$

The ψ_{100} are the Hydrogenic wave fct for $H(Z) = \frac{p^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}$

From the virial thm
$$\left.\begin{aligned} \langle\psi_{n\ell m}|\tfrac{p^2}{2m}|\psi_{n\ell m}\rangle &= -Z^2 E_n \\ \langle\psi_{n\ell m}|\tfrac{-Ze^2}{4\pi\epsilon_0 r}|\psi_{n\ell m}\rangle &= 2Z^2E_n \end{aligned}\right]$$
See Prob 4.48b

The 1st 4 terms of the Hamiltonian give

$$\langle\psi_{tr}|\frac{p_1^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} + \frac{p_2^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r}|\psi_{tr}\rangle = -2Z^2E_1 + 2\,(2Z2E_1) = (-2Z^2+8Z)\,E_1$$

I will calculate the $1/r_{12}$ matrix element using a different idea than the book

$$\langle\psi_{tr}|\frac{e^2}{4\pi\epsilon_0 r_{12}}|\psi_{tr}\rangle = \int \psi_{100}^2(r_1,Z)\,e\left[\int \psi_{100}^2(r_2,Z)\frac{e}{4\pi\epsilon_0 r_2}\,d^3\vec{r}_2\right]d^3r_1$$

The term in square brackets is the electric potential from the spherically symmetric density distribution $\rho(\vec{r}_2) = e\,\psi_{100}^2(r_2,Z)$

Argument for why $\vec{E}$ is spherically symmetric

$$E_r(r) = \frac{1}{4\pi\epsilon_0 r^2}\left[4\pi\int_0^r \rho(r')\,r'^2\,dr'\right]^{Q_{in}} = \frac{e}{\epsilon_0 r^2}\frac{Z^3}{\pi a_0^3}\int_0^r r'^2 e^{-2Zr'/a_0}\,dr'$$

$$= \frac{e}{4\pi\epsilon_0 r^2}\left[1 - e^{-2rZ/a_0}\left(1 + \frac{2rZ}{a_0} + \frac{2r^2Z^2}{a_0^2}\right)\right]$$

Now use $E_r = -\frac{\partial V}{\partial r}$ and integrate by parts

$$\langle\psi_{tr}|\frac{e^2}{4\pi\epsilon_0 r_{12}}|\psi_{tr}\rangle = \int Q_{ins}(r_1)\,E(r_1)\,dr_1 = \frac{e^2}{4\pi\epsilon_0}\int_0^\infty \frac{1}{r_1^2}\; 1 - e^{-2r_1Z/a_0}\left(1 + \frac{2r_1Z}{a_0} + \frac{2r_1^2Z^2}{a_0^2}\right)\Big]^2 dr_1$$

$$= \frac{2Ze^2}{4\pi\epsilon_0 a_0}\int_0^\infty \frac{1}{x^2}\left[1 - e^{-x}\left(1 + x + \frac{x^2}{2}\right)\right]^2 dx = \frac{2Ze^2}{4\pi\epsilon_0 a_0}\,\frac{5}{16} = -\frac{5}{4}Z\,E_1$$

Eq 8.32

Put all of the pieces together

$$\langle \psi_{tr} | H | \psi_{tr} \rangle = \left(-2Z^2 + 8Z - \tfrac{5}{4}Z\right) E_{100} \equiv E_{tr}$$

How to find the best Z?

$$\frac{\partial E_{tr}}{\partial Z} = -4Z + 8 - 5/4 = 0 \qquad Z = \frac{27}{16} \simeq 1.69$$

$$E_{tr} = \left(-2\left(\frac{27}{16}\right)^2 + \frac{27}{4}\,\frac{27}{16}\right) E_1 = \frac{1}{2}\left(\frac{3}{2}\right)^6 E_1 \simeq -77.5\,\text{eV} \qquad \sim 2\% \text{ error}$$

He requires 24.59 eV to ionize] He binding energy
He^+ " 54.42 " " 79.01 eV

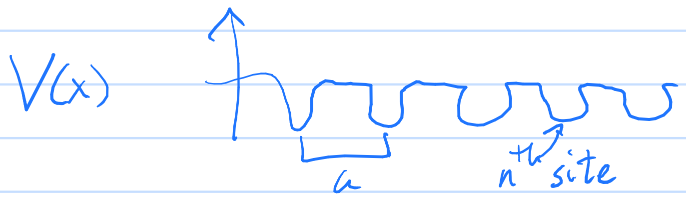
The ultrahigh accuracy currently achieved by large basis sets <u>and</u> understanding of ψ as $r_1 \to 0$ and/or $r_2 \to 0$ and/or $r_{12} \to 0$

The main physical effect missing is electron correlation. There tends to be less probability at $r_{12} \sim$ small for given $r_1 + r_2$
Our wave fct. misses this effect completely

See the book for H_2^+

Last case to look at: why does it seem that electrons can almost freely travel through some solids? The ions/atoms seem like they should scatter the electron over distance scale ~ 1-10 Å

Tight Binding Approximation Look into the case where the electron is localized to one site to a good approximation.



N sites total

Use a trial wave fct consisting of basis functions localized to each of the sites.

$y_j(x) = f(x - x_j)$ $\qquad\qquad$ $\Psi_{tr,n} = y_1(x)\, a_{1,n} + y_2(x)\, a_{2,x} + \dots$

From the variational principle with linear coefficients

$$\underline{\underline{H}}\, \vec{a}_n = E_{tr,n}\, \vec{a}_n$$

In the tight binding approximation,

$$\int_{-\infty}^{\infty} y_j(x)\, y_{j'}(x)\, dx = \delta_{jj'}$$

$$H_{j,j} \equiv \int_{-\infty}^{\infty} y_j(x)\, H\, y_j(x)\, dx \equiv \mathcal{E}_0$$

$$H_{j,j\pm1} = \int_{-\infty}^{\infty} y_j(x)\, H\, y_{j\pm1}(x) \equiv -V$$

$$H_{j,j\pm\Delta j} = 0 \quad \text{for} \quad |\Delta j| \geq 2$$

only the nearest sites in H

Note − sign

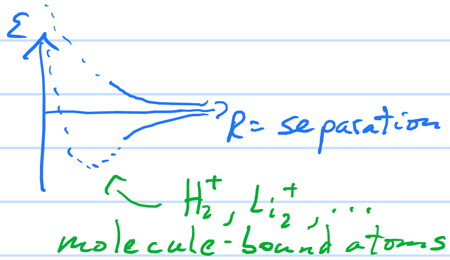
V = hopping amplitude

why $\mathcal{E}_0$ doesn't depend on j?

Two sites $\qquad$ $\begin{pmatrix} \mathcal{E}_0 & -V \\ -V & \mathcal{E}_0 \end{pmatrix} \begin{pmatrix} a_{1,n} \\ a_{2,n} \end{pmatrix} = \mathcal{E}_n \begin{pmatrix} a_{1,n} \\ a_{2,n} \end{pmatrix}$

$\mathcal{E}_{\pm} = \mathcal{E}_0 \mp V$ $\qquad$ $\vec{a}_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$

$|V|$ increases as atoms get closer



H_2^+, Li_2^+, ...
molecule-bound atoms

For solids, the number of sites ~ really huge. Can take the number of sites to be N→∞. In this case what happens at the boundary (j=0 and j=N+1) not important. Approximate as a ring

$$H = \begin{pmatrix} \mathcal{E}_0 & -V & & -V \\ -V & \mathcal{E}_0 & -V & \\ 0 & -V & \ddots & \\ -V & & & \end{pmatrix}$$

Note the V in the corner. Like saying $a_{0,n} = a_{N,n}$

$$-V\, a_{j-1,n} + \mathcal{E}_0\, a_{j,n} + -V\, a_{j+1,n} = \mathcal{E}_n\, a_{j,n}$$

Since there's nothing to make site j special guess the form

$a_{j,n} = \frac{1}{\sqrt{N}} e^{i\beta_n j}$

How to tell if this is a solution?

$$-V\frac{1}{\sqrt{N}} e^{i\beta_n j} e^{-i\beta_n} + \varepsilon_0 \frac{1}{\sqrt{N}} e^{i\beta_n j} + -V\frac{1}{\sqrt{N}} e^{i\beta_n j} e^{i\beta_n} = \varepsilon_n \frac{1}{\sqrt{N}} e^{i\beta_n j}$$

$$\varepsilon_n = \varepsilon_0 - 2V\cos\beta_n$$

How to determine the β_n? $a_{0,n} = a_{N,n}$ $1 = e^{i\beta_n N}$

Two equivalent ways to get all of the values:

$\beta_n = \frac{2\pi}{N} n$ $n = 1, 2, \ldots N$ or $n = 0, 1, 2, \ldots N-1$ why the same?

OR

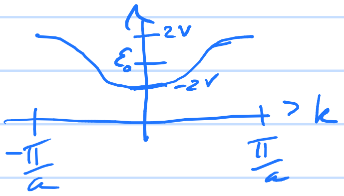
$\beta_n = \frac{2\pi}{N} n$ $n = -\frac{N-1}{2}, -\frac{N-3}{2}, \ldots -1, 0, 1, \ldots \frac{N-3}{2}, \frac{N-1}{2}$ $N =$ odd

$= -\frac{N-2}{2}, -\frac{N-4}{2}, \ldots -1, 0, 1, \ldots \frac{N-2}{2}, \frac{N}{2}$ $N =$ even

The second case is more typical because it looks like momentum states

$P_n = \frac{\hbar}{a}\beta_n$ Lattice momentum

$k_n = \frac{1}{a}\beta_n$



Show band structure plots.

What determines electrical conductors/insulators/etc?

If you don't want wrap bdry conditions, imagine the lattice going to 0 and N+1 with bdry conds. $a_{0,n} = 0$, $a_{N+1,n} = 0$

$a_{j,n} = \sqrt{\frac{2}{N}} \sin(\beta_n j)$ $\beta_n = \frac{n\pi}{N+1}$ $n = 1, 2, 3, \ldots N$

$\varepsilon_n = \varepsilon_0 - 2V\cos(\beta_n)$

Note that wrap conditions gives most states doubly degenerate while fixed bdry cnds gives all states non degenerate.

The "density of states" are the same in the limit $N \to \infty$