Infinite 1-D Lattice I

CTDL, pages 1156-1168

LAST TIME:

hole ($\hbar^+$) vs. e^- configurations — $\ell^N \leftrightarrow \ell^{2(2\ell+1)-N}$ [e.g. $f^{13} \leftrightarrow f^1$] for $N > 2\ell + 1$

e^2/r_{ij} unchanged

$\zeta(\text{NLS}) \leftrightarrow -\zeta(\text{NLS})$ — [$\zeta_{n\ell}$ unchanged]

Hund's 3rd Rule (Lowest L-S term of ℓ^N only)

$N<2\ell+1$	E_{MIN} for $J = \lvert L-S \rvert$	regular
$N=2\ell+1$	${}^{(2\ell+1)+1}S_{J=\frac{2\ell+1}{2}}$	S state: no fine structure
$N>2\ell+1$	E_{MIN} for $J = L+S$	inverted

Zeeman Effect

Wigner-Eckart Theorem used to define g_J

$$E^{Zeeman} = -\mu_0 M_J g_J B_Z$$

equal spacings

g_J as L,S,J diagnostic

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Confirm by $\mathbf{H}^{Zeeman}$ in Slater determinantal basis

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TODAY:

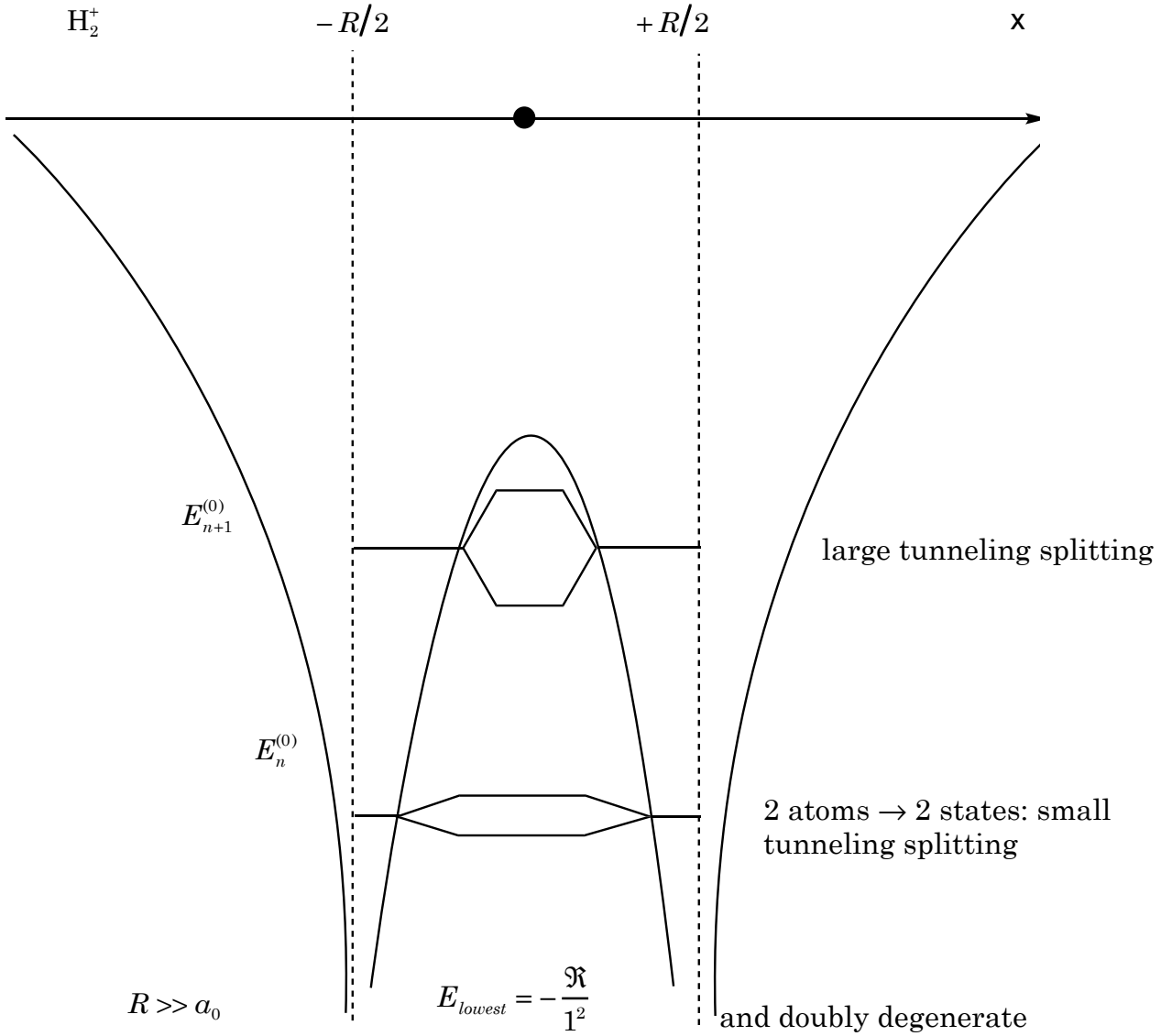
1. H_2 as example of localization, delocalization, tunneling
2. ∞ dimension secular equation for simplified 1-D lattice
3. eigenvectors by equal probability trick
4. restrict k to $|k| < \pi/\ell$: 1st Brillouin Zone
5. $E(k) = E_0 - 2A\cos k\ell$ (are these all of the allowed states?)
6. Bloch functions $\psi_k(x) = e^{ikx}\mu_k(x)$

next lecture

7. wavepackets, motion, group velocity
8. transitions: energy bands and intensity profiles
9. conductivity

Start with H_2^+, a lattice with only 2 equivalent sites.

qualitative picture: atomic energy levels
tunneling between identical localized states:
is slow behind a high barrier (small splitting)
is fast behind a low barrier (large splitting)
levels → bands, of width related to tunneling rate



For exact degeneracy between left-well and right-well localized states, can choose any linear combination

Localized basis set: $\psi_{\text{localized}} = \psi_{\text{left}}^{(0)}$ or $\psi_{\text{right}}^{(0)}$

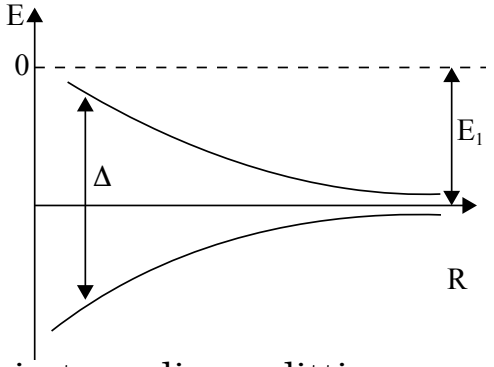
Delocalized basis set $\psi_{\textit{de}\text{localized}} = 2^{-1/2}\left[\psi_{\text{left}}^{(0)} \pm \psi_{\text{right}}^{(0)}\right]$

If initially in a localized state, tunneling rate depends on

* height (relative to $E_n^{(0)}$) of barrier
* width of barrier
* size of overlap between exponential tails of $\psi_{\text{left}}^{(0)}$ and $\psi_{\text{right}}^{(0)}$

clear that tunneling rate (i.e. reciprocal of adjacent level-splitting) increases

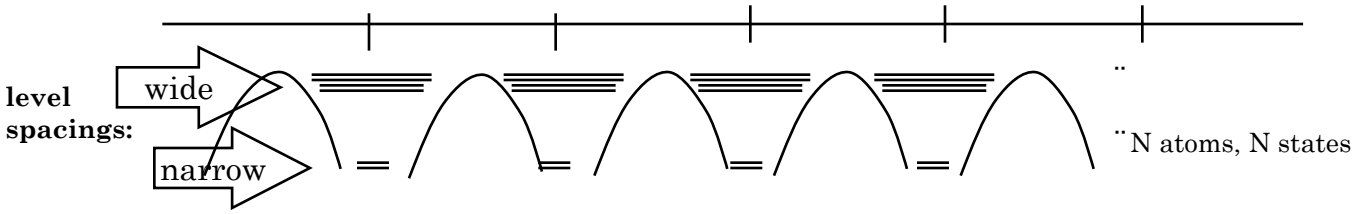
* as n↑ at constant R (internuclear separation)
* as R↓ at constant n



double degeneracy
at $R \to \infty$

Δ is tunneling splitting — gets larger as R↓. Less localization causes tunneling rate to increase. The tunneling rate is $\frac{\Delta E}{h}$ (which has units of 1/t).

N ATOMS ALONG A STRAIGHT LINE



Each electronic state of the isolated atom becomes a band of states for ∞–atom lattice. Energy width of each band increases as the principal quantum number increases because atomic states require more room: $\langle r \rangle_n \propto a_0 n^2$. Tunneling gets faster. Greater sensitivity to the world outside a single atom.

Simplified model for ∞ 1–Dimensional Lattice: basis for qualitative insights and early-time predictions.

1. Each ion, called q, has **one** bound state, $|\nu_q\rangle$
   at $E_0 = \langle\nu_q|\mathbf{H}|\nu_q\rangle$ [diagonal element of **H**] (actually 2 spin-orbitals)

2. Only permit orbitals on *adjacent* ions to interact [important simplifying assumption], like Hückel theory.

3. symmetry: all ions are equally spaced, $x_{q+1} - x_q = \ell$, and all adjacent-orbital interaction matrix elements are identical

$\langle\nu_q|\mathbf{H}|\nu_{q+1}\rangle \equiv -A$ [off-diagonal elements of **H**]
[reasons for – A sign choice later.]

(|A| must increase as $\ell \to 0$)

$$\text{so } \mathbf{H} = \begin{pmatrix} E_0 & -A & & \mathbf{0} \\ -A & \ddots & \ddots & \\ & \ddots & E_0 & -A \\ \mathbf{0} & & -A & \ddots \\ & & & \ddots \end{pmatrix}$$

tridiagonal infinite matrix

Since this is infinite, we need a trick to diagonalize it.

try a general variational function

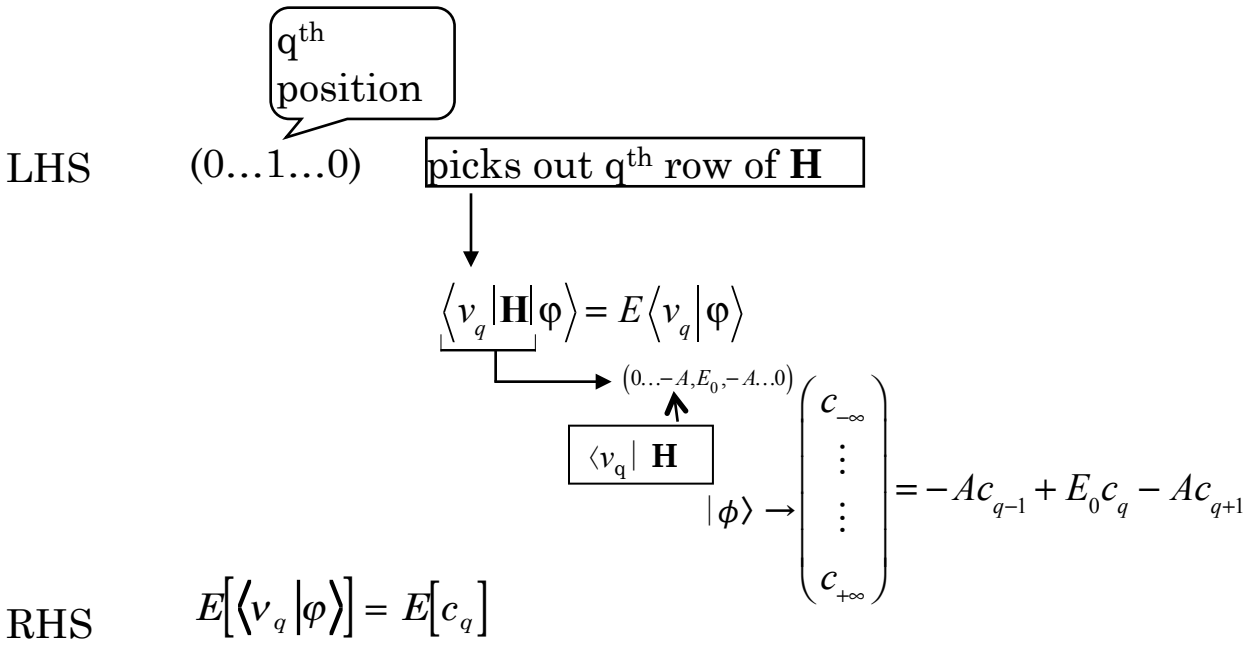
$$|\varphi\rangle = \sum_{q=-\infty}^{\infty} c_q |\nu_q\rangle$$

superposition of AO's each localized at each site

we get requirements on c_q by plugging this into the Schrödinger equation

$$\mathbf{H}|\varphi\rangle = E|\varphi\rangle$$

left multiply by $\langle\nu_q|$



$$0 = c_q\left[E_0 - E\right] - c_{q-1}A - c_{q+1}A$$

comes from the assumed simple form of the model

TRICK: probability of finding e^- on each lattice site should be the same for all sites (complex amplitudes might differ but the probabilities will be constant)

let $\boxed{c_q = e^{ikq\ell}}$ $\quad |c_q|^2 = 1$ for all q

This choice of c_q is a good guess that is consistent with expectation of equal probabilities on each lattice site.

ℓ is the distance between adjacent atoms
q is an integer
$q\ell$ is the coordinate of the q-th site: looks like an e^{ikx} plane wave
k is of dimension ℓ^{-1}

This problem reduces to finding the allowed values of k.

The periodicity of the lattice provides the important result, that if k is replaced by k', where $k' = k + \frac{2\pi}{\ell}$, the wavefunction does not change (translational symmetry).

$$c'_q = e^{ik'q\ell} = e^{\left(ikq\ell + i\frac{2\pi}{\ell}\ell\right)} = e^{ikq\ell}\underbrace{e^{i2\pi q}}_{=1} = c_q$$

Since all distinguishable $|\varphi\rangle$ may be generated by choosing the value of k in the interval $-\frac{\pi}{\ell} \le k < \frac{\pi}{\ell}$, restrict k to this range; **this range of k is called the "First Brillouin zone".**

Return to question about what happens when E is not in the range allowed by this range of k. Then E is not in the 1st Brillouin Zone. Next lecture [get another part of the band structure using qualitative perturbation theory rather than a matrix diagonalization calculation].

Plug $c_q = e^{ikq\ell}$ into Schrödinger Equation

$$0 = c_q\left(E_0 - E\right) - A\left(c_{q+1} + c_{q-1}\right)$$

$$0 = e^{ikq\ell}\left(E_0 - E\right) - A\left(e^{ik(q+1)\ell} + e^{ik(q-1)\ell}\right)$$

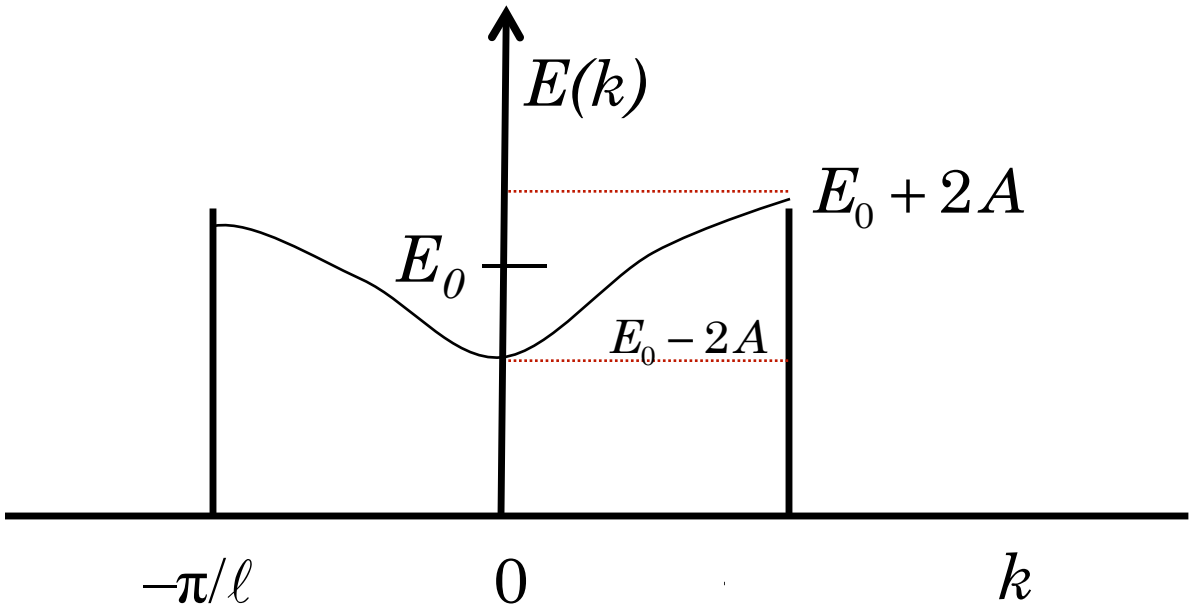
divide by $e^{ikq\ell}$ and rearrange

$$E = E_0 - A\underbrace{\left[e^{ik\ell} + e^{-ik\ell}\right]}_{2\cos k\ell}$$

This is the condition on E,k that must be satisfied for all eigenfunctions of the Schrödinger equation!

$$\boxed{E = E_0 - 2A\cos k\ell}$$

E varies continuously over finite interval $E_0 \pm 2A$



The choice $\left\langle \nu_q \left| \mathbf{H} \right| \nu_{q+1} \right\rangle = -A$ leads to a minimum E at $k = 0$.

Are these *all* of the allowed energy levels that arise from a single orbital at each lattice site? Apparently not — see Lecture #38. They are only half of the states. [One orbital per atom → two spin-orbitals per atom. Antisymmetrization gives another separate band.] like singlet vs. triplet.

We could repeat the calculation looking for a higher energy state at each site. Would get a broader band centered at higher energy.

Take a closer look at the spatial form of $\varphi_k(x) \equiv \langle x | \varphi_k \rangle$

$$\varphi_k(x) = \left\langle x \middle| \varphi_k \right\rangle = \sum_{q=-\infty}^{+\infty} e^{ikq\ell} \underbrace{\left\langle x \middle| \nu_q \right\rangle}_{\nu_q(x)}$$

treated as sum over localized functions

The goal is to replace the infinite sum by a single term:

This is called a Bloch function

show that: $\varphi_k(x) \sim \overbrace{e^{ikx} u_k(x)}$

plane wave (Free particle)

periodicity of lattice

Begin by requiring that $\varphi_k(x) = \sum_{q=-\infty}^{\infty} e^{ikq\ell} \nu_q(x)$

Translational symmetry imposes a relationship between $\nu_q(x)$ and $\nu_0(x)$

each $\nu_q(x)$ is localized at site q.

This is a single function rather than a sum of separate localized functions.

$$\nu_q(x) = \nu_0\left(x - q\ell\right)$$

$$\varphi_k(x) = \sum_{q=-\infty}^{\infty} e^{ikq\ell} \nu_0\left(x - q\ell\right)$$

shift x by $-q\ell$ to get from site q to site 0

$$\varphi_k(x+\ell) = \sum_{q=-\infty}^{\infty} e^{ikq\ell} \underbrace{\nu_0\left(x + \ell - q\ell\right)}_{=\nu_0(x-(q-1)\ell)}$$

$$= e^{ik\ell} \sum_{q=-\infty}^{\infty} e^{ik(q-1)\ell} \nu_0\left(x - (q-1)\ell\right)$$

Re-index the sum (replace q–1 by q) get original function multiplied by $e^{ik\ell}$

$$\varphi_k(x+\ell) = \underbrace{e^{ik\ell}}_{\text{translation by } \ell}\varphi_k(x)$$

This form of ϕ_k has all of the symmetry properties we will need. This form is sufficient to satisfy the symmetry requirements (boundary conditions). This means, instead of writing $\varphi_k(x)$ as sum over atom-localized $v_q(x)$'s, it is possible to write $\varphi_k(x)$ for all k as a product of 2 factors.

$$\varphi_k(x) = e^{ikx}u_k(x)$$

this has the properties of the above sum form, but is more general

1st factor conveys translational symmetry of a plane wave with wavevector k, 2nd factor builds in translational symmetry of a lattice with spacing ℓ. This is a more general expression that incorporates all of the properties of the original definition of $\varphi_k(x)$ as a sum over localized orbitals.

$$u_k(x+\ell) = u_k(x)$$

note that

$$\varphi_k(x+\ell) = e^{ikx}e^{ik\ell}u_k(x+\ell) = e^{ik\ell}\left[e^{ikx}u_k(x)\right]$$

$$= e^{ik\ell}\varphi_k(x)$$

as required.

Note also that $|\varphi_k(x+n\ell)|^2 = |\varphi_k(x)|^2$ implies that, as required, the e^- has equal probability of being found on each site.

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