Infinite 1-D Lattice

CTDL, pages 1156-1168

LAST TIME:

hole (h^+) vs. e^- configurations: $\ell^N \leftrightarrow \ell^{2(2\ell+1)-N}$ for $N > 2\ell+1$

e^2/r_{ij} unchanged

$\zeta(NLS) \rightarrow -\zeta(NLS)$ $\left[\zeta_{n\ell} \text{ unchanged}\right]$

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:

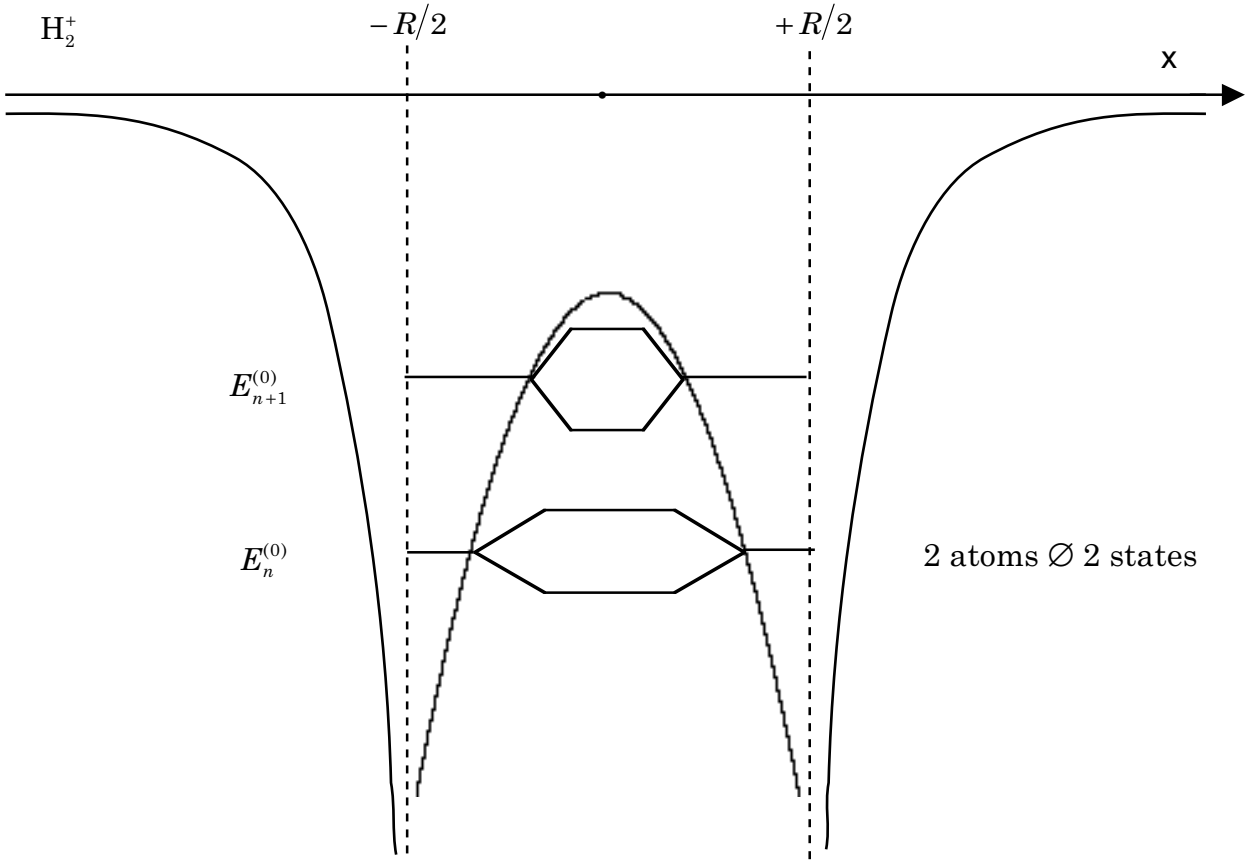
1. H_2^+ as example of localization, delocalization, tunneling
2. ∞ secular equation for simplified 1-D lattice
3. eigenvectors by equal probability trick
4. restrict k to $\lvert k \rvert < \pi/\ell$: 1st Brillouin Zone
5. $E(k) = E_0 - 2A\cos k\ell$ (all of the allowed states?)
6. Bloch functions $\psi_k(x)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

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
slow behind big barrier (small splitting)
fast behind small barrier (large splitting)
levels → bands, of width related to tunneling rate



$R >> a_0$ $E_{lowest} = -\frac{\Re}{1^2}$ and doubly degenerate

for exact degeneracy, can choose any linear combination

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

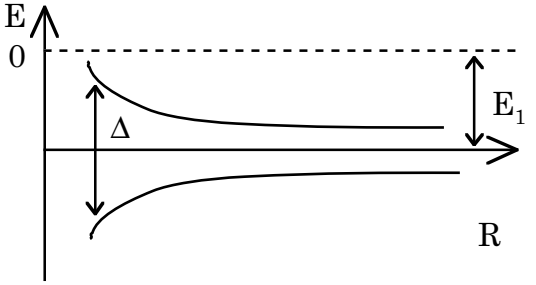
Delocalized basis set $\psi_{\text{delocalized}} = 2^{-1/2}\left[\psi_{\text{left}}^{(0)} \pm \psi_{\text{right}}^{(0)}\right]$

If initially in localized state, tunneling rate depends on

* height $\left(\text{relative to } E_n^{(0)}\right)$ 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. splitting) increases

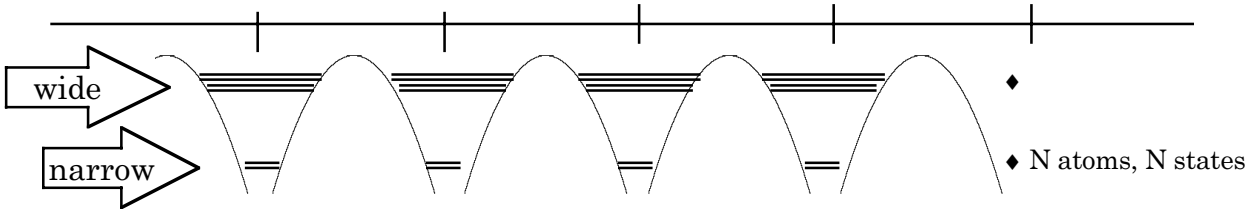
* as n↑ at constant R (internuclear separation)
* as R↓ at constant n



double degeneracy
at $R \to \infty$

Δ is tunneling splitting—gets larger as R↓

N ATOMS ALONG A STRAIGHT LINE



each electronic state of isolated atom becomes band of states for ∞ lattice.

Energy width of each band increases as the principal q.n. increases because atomic states require more room: $\langle r \rangle_n \propto a_0 n^2$. Tunneling gets faster.

Greater sensitivity to world outside one 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. permit orbitals only on adjacent ions to interact [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

$$\langle\nu_q|\,\mathbf{H}\,|\nu_{q+1}\rangle \equiv -A \qquad \text{[off-diagonal elements of H]}$$

($\Im A \Im$ would increase as $\ell \to 0$) [reasons for – A sign choice later.]

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, need a trick to diagonalize it.

general variational function

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

superposition of AO's at each site

get requirements on c_q by plugging this into Schrödinger equation

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

left multiply by $\langle\nu_q|$

LHS $(0\ldots1\ldots0)$ (q'th position) picks out q-th row of **H**

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

$$(0\ldots -AE_0 - A \ldots 0) \begin{pmatrix} c_{-\infty} \\ \vdots \\ \vdots \\ c_{+\infty} \end{pmatrix} = -Ac_{q-1} + E_0 c_q - Ac_{q+1}$$

RHS $E\left[\langle \nu_q | \varphi \rangle\right] = E\left[c_q\right]$

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

comes from the assumed simple form of model

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

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

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

ℓ is distance between adjacent atoms
q is integer
$q\ell$ is the coordinate of the q-th site: looks like e^{ikx} plane wave
k is of dimension ℓ^{-1} (problem reduces to finding allowed values of k.)

periodicity of 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)

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

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

Return to question about what happens when k is not in 1st Brillouin Zone next time [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

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

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

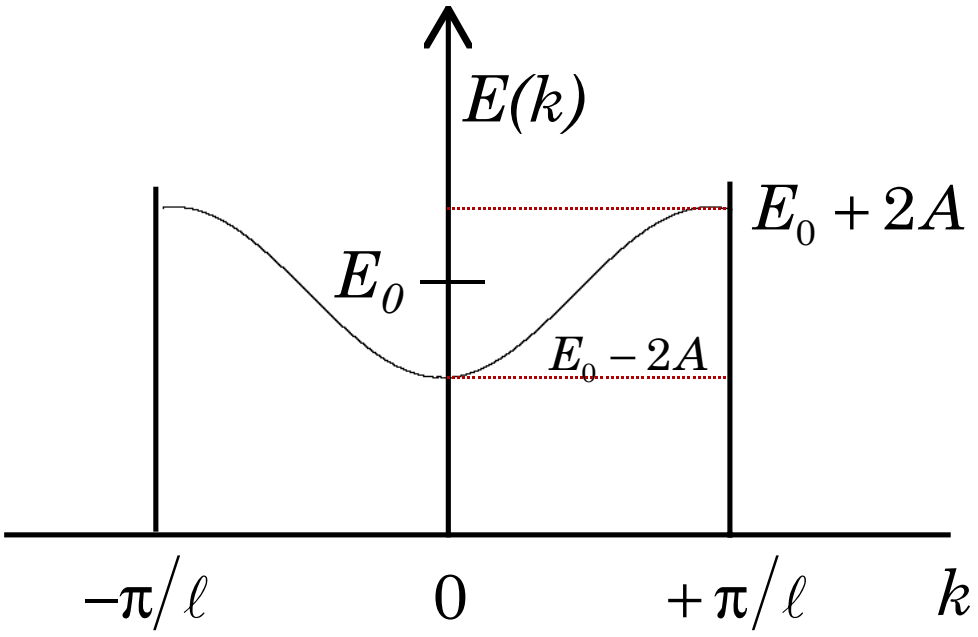
divide by $e^{ikq\ell}$ and rearrange

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

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

$$E = E_0 - 2A\cos k\ell$$

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



The choice $\langle \nu_q | \mathbf{H} | \nu_{q+1} \rangle = -A$ leads to 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 next time. Only half of the states. [One orbital per atom → two spin-orbitals per atom. Antisymmetrization gives another separate band.]

Could repeat calculation for a higher energy state at each site. Would get a broader band centered at higher energy.

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

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

goal is to replace infinite sum by single term:

show that: $\varphi_k(x) \sim \overbrace{e^{ikx} u_k(x)}^{\text{This is called a Bloch function}}$

plane wave (Free particle) — e^{ikx}

periodicity of lattice — $u_k(x)$

begin by requiring that $\varphi_k(x) = \sum_{q=-\infty}^{\infty} e^{ikql} \nu_q(x)$

Translational symmetry imposes a relationship between $\nu_q(x)$ and ν_0

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

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

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

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

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

$$= e^{ik\ell} \sum e^{ik(q-1)\ell} \nu_0(x - (q-1)\ell)$$

re-index sum (replace q–1 by q)

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

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 $\nu_q(x)$'s, it is possible to write $\varphi_k(x)$ as product of 2 factors

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

1st factor conveys translational symmetry of a plane wave with wavevector k, 2nd factor builds in translational symmetry of 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 $\Im\varphi_k(x + n\ell)\Im^2 = \Im\varphi_k(x)\Im^2$ implies that, as required, e^- has equal probability of being found on each site.