Infinite 1-D Lattice

CTDL, pages 1156-1168

LAST TIME:

hole \( h^+ \) vs. e⁻ configurations:

\[ \ell^N \leftrightarrow \ell^{2(\ell+1)-N} \text{ for } N > 2\ell + 1 \]

\[ e^2/r_{ij} \text{ unchanged} \]

\[ \zeta(\text{NLS}) \rightarrow -\zeta(\text{NLS}) \quad \text{[ } \zeta_{nl} \text{ unchanged} ] \]

Hund’s 3rd Rule (Lowest L-S term of \( \ell^N \) only)

\[ \begin{align*}
N < 2\ell + 1 & \quad E_{\text{MIN}} \text{ for } J = |L - S| & \text{regular} \\
N = 2\ell + 1 & \quad (2\ell+1)S \quad J = \frac{2\ell+1}{2} & \text{S state: no fine structure} \\
N > 2\ell + 1 & \quad E_{\text{MIN}} \text{ for } J = L + S & \text{inverted}
\end{align*} \]

Zeeman Effect

Wigner-Eckart Theorem used to define \( g_J \)

\[ E^{\text{Zeeman}} = -\mu_0 M_J g_J B_z \]

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

Confirm by \( H^{\text{Zeeman}} \) in Slater determinantal basis

TODAY:

1. \( H^+_2 \) as example of localization, delocalization, tunneling
2. \( \infty \) secular equation for simplified 1-D lattice
3. eigenvectors by equal probability trick
4. restrict \( k \) to \( |k| < \pi/\ell \) : 1st Brillouin Zone
5. \( E(k) = E_0 - 2A \cos k\ell \) (all of the allowed states?)
6. Bloch functions \( \psi_k(x) = e^{ikx}u_k(x) \)
7. wavepackets, motion, group velocity
8. transitions – energy bands and intensity profiles
9. conductivity

next lecture
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 $\rightarrow$ bands, of width related to tunneling rate

for exact degeneracy, can choose any linear combination

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

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

It is clear that tunneling rate (i.e. splitting) increases:
* as $n \uparrow$ at constant $R$ (internuclear separation)
* as $R \downarrow$ at constant $n$

$\Delta$ is tunneling splitting—gets larger as $R \downarrow$

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**N ATOMS ALONG A STRAIGHT LINE**

Each electronic state of isolated atom becomes band of states for $\infty$ 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 $\infty$ 1–Dimensional Lattice: basis for qualitative insights and early time predictions.

1. Each ion, called $q$, has one bound state, $|v_q\rangle$
   
   at $E_0 = \langle v_q | H | v_q \rangle$ [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

   $\langle v_q | H | v_{q+1} \rangle \equiv -A$ [off-diagonal elements of $H$]
   
   (3A3 would increase as $\ell \to 0$) [reasons for $-A$ sign choice later.]

   so

   $$H = \begin{pmatrix} E_0 & -A & 0 & \cdots \\ -A & E_0 & -A & \cdots \\ 0 & -A & E_0 & -A & \cdots \\ \vdots & \vdots & \vdots & \ddots & \ddots \end{pmatrix}$$

   [tridiagonal infinite matrix]

   since this is infinite, need a trick to diagonalize it.

   general variational function

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

   superposition of AO's at each site

   get requirements on $c_q$ by plugging this into Schrödinger equation

   $$H|\varphi\rangle = E|\varphi\rangle$$

   left multiply by $\langle v_q |$
LHS \( (0\ldots1\ldots0) \) picks out q-th row of \( H \)

\[
\langle \nu_q | H | \varphi \rangle = E \langle \nu_q | \varphi \rangle
\]

\[ (0\ldots-AE_0\ldots0) \]

\[
\begin{pmatrix}
  c_{-\infty} \\
  \vdots \\
  c_{1} \\
  \vdots \\
  c_{\infty}
\end{pmatrix} = -A c_{q-1} + E_0 c_q - A c_{q+1}
\]

RHS \( E[\langle \nu_q | \varphi \rangle] = E[c_q] \)

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

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)

Let \( c_q = e^{ikq\ell} \)

\[ |c_q|^2 = 1 \quad \text{for all } q \]

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

\( \ell \) 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 \( \ell^{-1} \)

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)
\[ c'_q = e^{ik'q \ell} = e^{\left(ikq\ell + \frac{2\pi}{\ell} q\ell \right)} = e^{ikq\ell} e^{i2\pi q} = c_q \]

Since all distinguishable \(|\varphi\rangle\) may be generated by choosing \(k\) in the interval \(-\frac{\pi}{\ell} \leq k < \frac{\pi}{\ell}\), 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

\[
0 = c_q (E_0 - E) - A(c_{q+1} + c_{q-1})
\]

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

divide by \(e^{ikq\ell}\) and rearrange

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

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 $\langle \psi_q | H | \psi_{q+1} \rangle = -A$ 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 $\rightarrow$ 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.
closer look at spatial form of $\varphi_k(x) \equiv \langle x \mid \varphi_k \rangle$

$$\varphi_k(x) = \langle x \mid \varphi_k \rangle = \sum_{q=-\infty}^{\infty} e^{ikq} \langle x \mid v_q \rangle_{v_q(x)}$$

goal is to replace infinite sum by single term:

This is called a Bloch function

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

plane wave (Free particle) \hspace{1cm} periodicity of lattice

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

Translational symmetry imposes a relationship between $v_q(x)$ and $v_0$

each $v_q(x)$ is localized at site $q$.

$$v_q(x) = v_0(x - q\ell)$$

$$\varphi_k(x) = \sum_{q=-\infty}^{\infty} e^{ikq} v_0(x - q\ell)$$

$$\varphi_k(x + \ell) = \sum_{q=-\infty}^{\infty} e^{ikq} \frac{v_0(x + \ell - q\ell)}{= v_0(x - (q-1)\ell)}$$

$$= e^{i k \ell} \sum e^{i k (q-1) \ell} v_0(x - (q-1)\ell)$$

shift $x$ by $-q\ell$ to get from site $q$ to site 0
re-index sum (replace q–1 by q)

\[ \varphi_k(x + l) = e^{i k \ell} \varphi_k(x) \]

This form of \( \varphi_k \) 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

\[ \varphi_k(x) = e^{i k x} u_k(x) \]

1st factor conveys translational symmetry of a plane wave with wavevector \( k \), 2nd factor builds in translational symmetry of lattice with spacing \( \ell \). 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.

\[ u_k(x + l) = u_k(x) \]

Note that

\[ \varphi_k(x + l) = e^{i k x} e^{i k \ell} u_k(x + l) = e^{i k \ell} [e^{i k x} u_k(x)] = e^{i k \ell} \varphi_k(x) \]

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.