PY4T01 Condensed Matter Theory

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PY4T01 Condensed Matter Theory

1. Introduction: What Hamiltonian? Born-Oppenheimer Approximation
2. Tight-binding method for molecules
3. From molecules to solid
4. Going from 1D to 2D and 3D
5. C-graphite and C-nanotubes
6. Interfaces: charge transfer and screening
7. A proper calculation: the Coulomb potential back
8. The Many-Body problem
9. The Hubbard model
10. The mean field approximation
11. Functional Theory
12. Density Functional Theory on a Lattice

1. Electronic transport: Classical model
2. Quantum Transport
3. Transfer matrix theory
4. Disorder and localization

Text Books

General Text:

1. *Electronic Structure of Materials*, A. P. Sutton, (Oxford University Press, 1996, ISBN 0-19-851754-8)
2. *Bonding and Structure of Molecules and Solids*, D. G. Pettifor, (Oxford University Press, 2002, ISBN 0-19-851786-6)

Additional:

1. *The Solid State*, H.M. Rosenberg, (Oxford University Press, 2003, ISBN 0-19-851870-6)
2. *Band Theory and Electronic Properties of Solids*, J. Singleton, (Oxford University Press, 2003, ISBN 0-19-850644-9)
3. *Solid State Physics*, N.W. Ashcroft and N.D. Mermin, (International Thomson Publishing, ISBN 0030839939)

Very Advanced:

1. *Quantum Theory of Many-Particle Systems*, J.D. Walecka and A.L. Fetter, (McGraw Hill College, 1971, ISBN 0070206538, also Dover Pubns, 2003, ISBN 0486428273)

Transport:

1. *Electronic Transport in Mesoscopic Systems*, S. Datta, (Cambridge University Press, 1995, ISBN 0521416043)

Density Functional Theory:

1. *Density-Functional Theory of Atoms and Molecules*, R.G. Parr and W. Yang, (Oxford University Press, 1994, ISBN 0195092767)

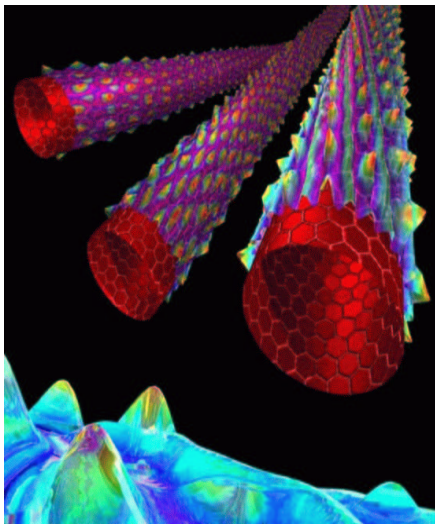
Other resources:

1. Research and Review Articles (distributed in class)

Why doing Condensed Matter Theory?

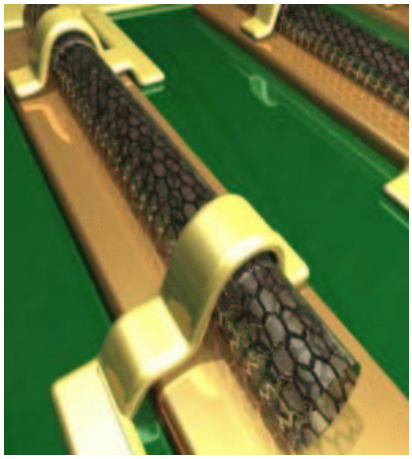
The main idea is to solve REAL problems!!!

- Is it a metal or a semiconductor?
- Why it is so tough?
- How do electrons propagate?



and to make predictions!!!

- Can it be magnetic?
- Can I build a transistor with it?
- How can I use it?
- What if ....



What Hamiltonian?

You have to decide the minimal Hamiltonian for the specific problem

1. Free-electrons
$$\mathcal{H} = -\frac{\hbar^2\nabla^2}{2m}$$

2. Electrons in periodic potential
$$\mathcal{H} = -\frac{\hbar^2\nabla^2}{2m} + V(\vec{r})$$

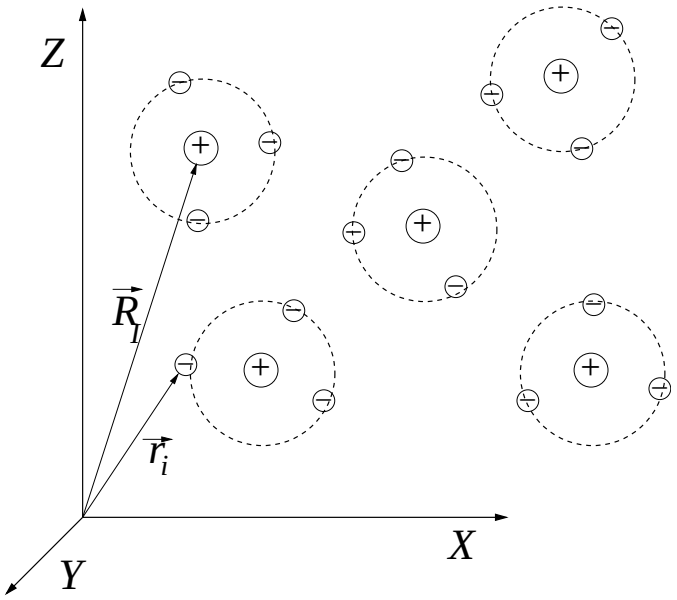
3. Hubbard Hamiltonian
$$\mathcal{H} = \epsilon_0 \sum_i n_i - t \sum_{i,j,\sigma} \left[c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma} \right] + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

4. Heisenberg Hamiltonian
$$\mathcal{H} = \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

5. Ising Hamiltonian
$$\mathcal{H} = \sum_{i,j} J_{ij} S_{zi} S_{zj}$$

6. .... Hamiltonian
$$\mathcal{H} = ...$$

Consider a system of N electrons and M nuclei.



Quantum Mechanics has given us a method to write the general Hamiltonian for such a system. Simply consider the classical Hamiltonian (*non-relativistic*):

$$H_{\text{classical}} = \sum_J^M \frac{P_J^2}{2M_J} + \frac{1}{2}\sum_{I\neq J}^M \frac{e^2 Z_I Z_J}{R_{IJ}} + \sum_j^N \frac{p_j^2}{2m_j} + \frac{1}{2}\sum_{i\neq j}^N \frac{e^2}{r_{ij}} - \frac{1}{2}\sum_{i,I}^{N,M} \frac{e^2 Z_I}{R_{iI}}$$

where $(R_{IJ} = |\vec{R}_I - \vec{R}_J| \quad R_{iI} = |\vec{r}_i - \vec{R}_I| \quad r_{ij} = |\vec{r}_i - \vec{r}_j|)$

R_J, P_J position and momentum nucleus J

r_j, p_j position and momentum electron j

Then Quantum Mechanics gives the prescription:

$$\begin{array}{ccc} \vec{R} & & \vec{R} \\ \vec{P}_i & \longrightarrow & -i\hbar\frac{\partial}{\partial R_i} \\ \vec{r} & & \vec{r} \\ \vec{p}_i & & -i\hbar\frac{\partial}{\partial r_i} \end{array}$$

Therefore the **GENERAL** Hamiltonian for a quantum mechanical system of N electrons and M nuclei is:

$$H(\vec{r},\vec{R}) = T_N(\vec{R}) + V_{NN}(\vec{R}) + T_e(\vec{r}) + V_{ee}(\vec{r}) + V_{eN}(\vec{r},\vec{R})$$

$T_N(\vec{R}) = -\sum_J^M \frac{\hbar^2\nabla_J^2}{2M_J}$ Nuclei kinetic Energy

$V_{NN}(\vec{R}) = \frac{1}{2}\sum_{I\neq J}^M \frac{e^2 Z_I Z_J}{R_{IJ}}$ Nucleus-Nucleus Interaction

$T_e(\vec{r}) = -\sum_j^N \frac{\hbar^2\nabla_j^2}{2m_j}$ Electrons kinetic Energy

$V_{ee}(\vec{r}) = \frac{1}{2}\sum_{i\neq j}^N \frac{e^2}{r_{ij}}$ Electron-Electron Interaction

$V_{eN}(\vec{r},\vec{R}) = -\frac{1}{2}\sum_{i,I}^{N,M} \frac{e^2 Z_I}{R_{iI}}$ Electron-Nucleus Interaction

You can divide H as follows

$$H(\vec{r}, \vec{R}) = H_e(\vec{r}) + H_N(\vec{R}) + V_{eN}(\vec{r}, \vec{R})$$

where we have introduce the nuclei

$$H_N(\vec{R}) = T_N(\vec{R}) + V_{NN}(\vec{R})$$

,

the electrons

$$H_e(\vec{r}) = T_e(\vec{r}) + V_{ee}(\vec{r})$$

,

and the interaction Hamiltonian

$$V_{eN}(\vec{r}, \vec{R})$$

Consider the size of the problem. Suppose we are describing ∼7gr of Li. This means we have to consider:

$$M \text{ nuclei} \sim 6 \times 10^{23}$$

$$N \text{ electrons} \sim 1.8 \times 10^{24}$$

So in order to describe properly 5gr of Li I have an equation with

$$\underline{3 \times \left[6 \times 10^{23} + 1.8 \times 10^{24}\right] = 7.2 \times 10^{24} \text{ variables}}$$

Than the wave function is

$$\Psi(\{\vec{R}\}, \{\vec{r}\}) \equiv \Psi(\vec{R}, \vec{r})$$

and the Schrödinger equation

$$H(\vec{r}, \vec{R})\Psi(\vec{R}, \vec{r}) = E\Psi(\vec{R}, \vec{r})$$

Obviously we must somehow reduce the problem.

Note that the dynamics of the electrons depends on that of the nuclei and viceversa, **NOT** *only on their relative positions*

Born-Oppenheimer Approximation

The nuclei (usually) move at a much slower speed than the electrons

- Nuclei: Sound Speed $v_S \sim 10^2 - 10^3$ m/s
- Electrons: Fermi Velocity $v_F \sim 10^5 - 10^6$ m/s

Electrons can always "adjust" their dynamics to that of the nuclei

$$\Psi(\{\vec{R}\},\{\vec{r}\}) = \phi(\{\vec{R}\})\psi(\{\vec{r}\};\{\vec{R}\}) \equiv \phi(\vec{R})\psi(\vec{r};\vec{R})$$

Electrons know about the nuclei only through their positions. So one can write:

$$H(\vec{R},\vec{r})\Psi(\vec{R},\vec{r}) = \phi(\vec{R})H_e(\vec{r})\psi(\vec{r}) + \psi(\vec{r})H_N(\vec{R})\phi(\vec{R}) + V_{eN}(\vec{r},\vec{R})\phi(\vec{R})\psi(\vec{r})$$

This is still not separable, however since $v_S \ll v_F$ we can write:

$$\left[T_e(\vec{r}) + V_{ee}(\vec{r}) + V_{eN}(\vec{r},\vec{R})\right]\psi(\vec{r}) = E(\vec{R})\psi(\vec{r})$$

$$\left[T_N(\vec{R}) + V_{NN}(\vec{R}) + E(\vec{R})\right] \phi(\vec{R}) = E_{tot}\phi(\vec{R})$$

One solves for electrons first (for each nuclei positions) and then for nuclei.

Born-Oppenheimer Approximation in more details

$$H_e\psi\phi + H_N\psi\phi + V_{eN}\psi\phi = E_{tot}\psi\phi$$

$$\left[\left(H_e + V_{eN}\right)\psi\right]\phi + \psi H_N\phi = E_{tot}\psi\phi$$

then the Born-Oppenheimer approximation says:

$$\left(H_e + V_{eN}\right)\psi = E(\vec{R})\psi$$

from which we obtain

$$\left[H_N + E(\vec{R})\right]\phi = E_{tot}\phi$$

Is the problem easier?

- YES, electrons and the nuclei can be treated almost independently
- Not all the nuclei positions are relevant
- Usually nuclei dynamics can be replaced by classical equations
- If I know where the nuclei are I can forget the last equation

Is the problem easy?

NO, I still have 10^{24} electrons

$$\left[T_e(\vec{r}) + V_{ee}(\vec{r}) + V_{eN}(\vec{r},\vec{R})\right]\psi(\vec{r}) = E(\vec{R})\psi(\vec{r})$$

In actual fact the REAL problem is the Coulomb term. Suppose it can be neglected then we have

$$\left[T_e(\vec{r}) + V_{eN}(\vec{r},\vec{R})\right]\psi(\vec{r}) = E(\vec{R})\psi(\vec{r})$$

The Hamiltonian is then separable and we have a set (1.8×10^{24}) of identical equations:

$$-\frac{\hbar^2\nabla^2}{2m}\psi(\vec{r}) - \frac{1}{2}\sum_I^M \frac{e^2 Z_I}{r_I}\psi(\vec{r}) = E\psi(\vec{r})$$

With the Coulomb interaction the dynamics of the i-th electron depends on that of the other $(1.8\times10^{24}-1)$ electrons

In what follows:

1. We will always use the Born-Oppenheimer approximation
2. In most of the cases we will neglect electron-electron interaction
3. At the end we will put electron-electron interaction back

In conclusion our present problem is to solve an equation of the form

$$-\frac{\hbar^2\nabla^2}{2m}\psi(\vec{r}) - \frac{1}{2}\sum_I^M \frac{e^2 Z_I}{r_I}\psi(\vec{r}) = E\psi(\vec{r})$$