

1.1. The many-body hamiltonian

$$H \Psi \equiv E \Psi; \Psi = \Psi(\{\vec{R}_I\}, \{\vec{r}_k\})$$

↑ positions of all nuclei
↑ positions & spins of all electrons

1) kinetic energy of the electrons

$$T^e = \sum_{k=1}^N \frac{p_k^2}{2m}$$

$$\vec{p}_k = \frac{\hbar}{i} \vec{\nabla}_{\vec{r}_k}$$

2) $T^{ion} = \sum_{I=1}^M \frac{p_I^2}{2M_I}$

$$\vec{p}_I = \frac{\hbar}{i} \vec{\nabla}_{\vec{R}_I}$$

3) electron-electron interaction N, N

$$V^{e-e}(\{\vec{r}_k\}) \approx \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k, k' \\ k \neq k'}} \frac{e^2}{|\vec{r}_k - \vec{r}_{k'}|}$$

has no spin/magnetism

4) ion-ion

$$V^{ion-ion}(\{\vec{R}_I\}) = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{I, J} \frac{e^2 Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

also has negatives
nuclear spin. = no prob.

5) electron-ion

$$V^{e-ion}(\{\vec{r}_\alpha, \delta_\alpha\}, \{\vec{R}_I\}) = \sum_{I=1}^M \sum_{k=1}^N v^{ion}(\vec{R}_I - \vec{r}_\alpha)$$

$v(\vec{r}_\alpha) =$ potential due to all ions
also called "external potential"

$$H = T^e + T^{ion} + V^{e-e} + V^{e-ion} + V^{ion-ion}$$

⇒ quite complex

How can we split this in easier to handle pieces?

1.2 Separating the dynamics of electrons and nuclei

or Born-Oppenheimer approximation

at first a "plausible" motivation

electrons are light & react fast to a perturbation (typically ~ 1 fs
femto = 10^{-15})

nuclei are heavier; they move on time scale of ~ 1 ps; pico = 10^{-12}

$$M_H/m = 1,840$$

$$M_{Si}/m = 28,086$$

$$M_{Kj}/m = 86,400$$

⇒ From electron point of view

nuclei hardly move
motion of electrons & of
nuclei (or ions) are not coupled

''' adiabatic principle
Born-Oppenheimer

Now exact treatment

electron hamiltonian: $H^e = T^e + V^{e-ion} + V^{e-e}$

$H = H^e + T^{ion} + V^{ion-ion}$

$$H^e(\{\vec{R}_I\}) \phi_\nu(\{\vec{R}_I\}; \{\vec{r}_k, \alpha_k\}) = E_\nu^e \phi_\nu$$

if $\frac{M_F}{m} \rightarrow \infty$ then H^e describes
the system

we use ϕ_ν as basis set.

$$\psi = \sum_\nu \Lambda_\nu(\{\vec{R}_I\}) \phi_\nu(\{\vec{R}_I\}; \{\vec{r}_k\})$$

$$H\psi = (H^e + T^{ion} + V^{ion-ion})\psi = \sum_\nu \Lambda_\nu E_\nu^e \phi_\nu$$

$$\begin{aligned}
 & + \Lambda_\nu \phi_0 v^{ion} + \\
 & T^{ion}(\Lambda_\nu \phi_0) \\
 \nabla_{\vec{R}_I}^2 (\Lambda_\nu \phi_0) = & \left(\nabla_{\vec{R}_I}^2 \Lambda_\nu \right) \cdot \phi_0 \\
 & + \Lambda_\nu \left(\nabla_{\vec{R}_I}^2 \phi_0 \right) \\
 & + 2 \left(\vec{\nabla}_{\vec{R}_I} \Lambda_\nu \right) \left(\vec{\nabla}_{\vec{R}_I} \phi_0 \right)
 \end{aligned}$$

Charge
rel

$$\langle \phi_\mu | H | \psi \rangle = E \Lambda_\mu =$$

$$\left(T^{ion} + E_\mu^e + v^{ion} - i0^+ \right) \Lambda_\mu$$

$$+ \sum_\nu \sum_{I=1}^M -\frac{\hbar^2}{2M_I} \left[\langle \phi_\mu | \nabla_{\vec{R}_I}^2 | \phi_\nu \rangle \Lambda_\nu$$

$$+ 2 \langle \phi_\mu | \vec{\nabla}_{\vec{R}_I} | \phi_\nu \rangle \left(\vec{\nabla}_{\vec{R}_I} \Lambda_\nu \right) \right]$$

still exact

→ = coupling between different states of H^e

these terms are called e-vibrational or e-phonon coupling.

If we calculate these terms
→ often these terms are
small.

Sometimes they are crucial

e.g. BCS - superconductivity,
Jahn-Teller, Peierls distortion,
Kohn - anomaly etc.

BO approx \equiv these terms are zero
" adiabatic
approx

$$(T^{\text{ion}} + V^{\text{ion-ion}} + E_{\mu}^e) \Delta_{\mu} = E_{\mu} \Delta_{\mu}$$

for $\mu = 0$: $V^{\text{ion-ion}} + E_{\mu}^e \equiv V^{\text{BO}}$

V^{BO} = Born-Oppenheimer
energy surface;
potential-energy surface

$\Delta_{\mu}(\{\vec{R}_I\})$ = strongly peaked
at positions of nuclei!

in principle ($T^{10n} \dots$) Δ_{μ}
 should be solved q.m. Doing so
 shows classical (Newton) treatment
 gives the result ... except for H
 even dimer is nearly
 classical.

e-vib terms nearly
 always neglected. O.K.
 for the past materials |

e-vib. coupling = timely
 and increasingly important field of
 research.

ground state = lowest energy state

$$E = E_0^e(\{\vec{R}_I\}) + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{I \neq J} \frac{e^2 z_I z_J}{|\vec{R}_I - \vec{R}_J|}$$

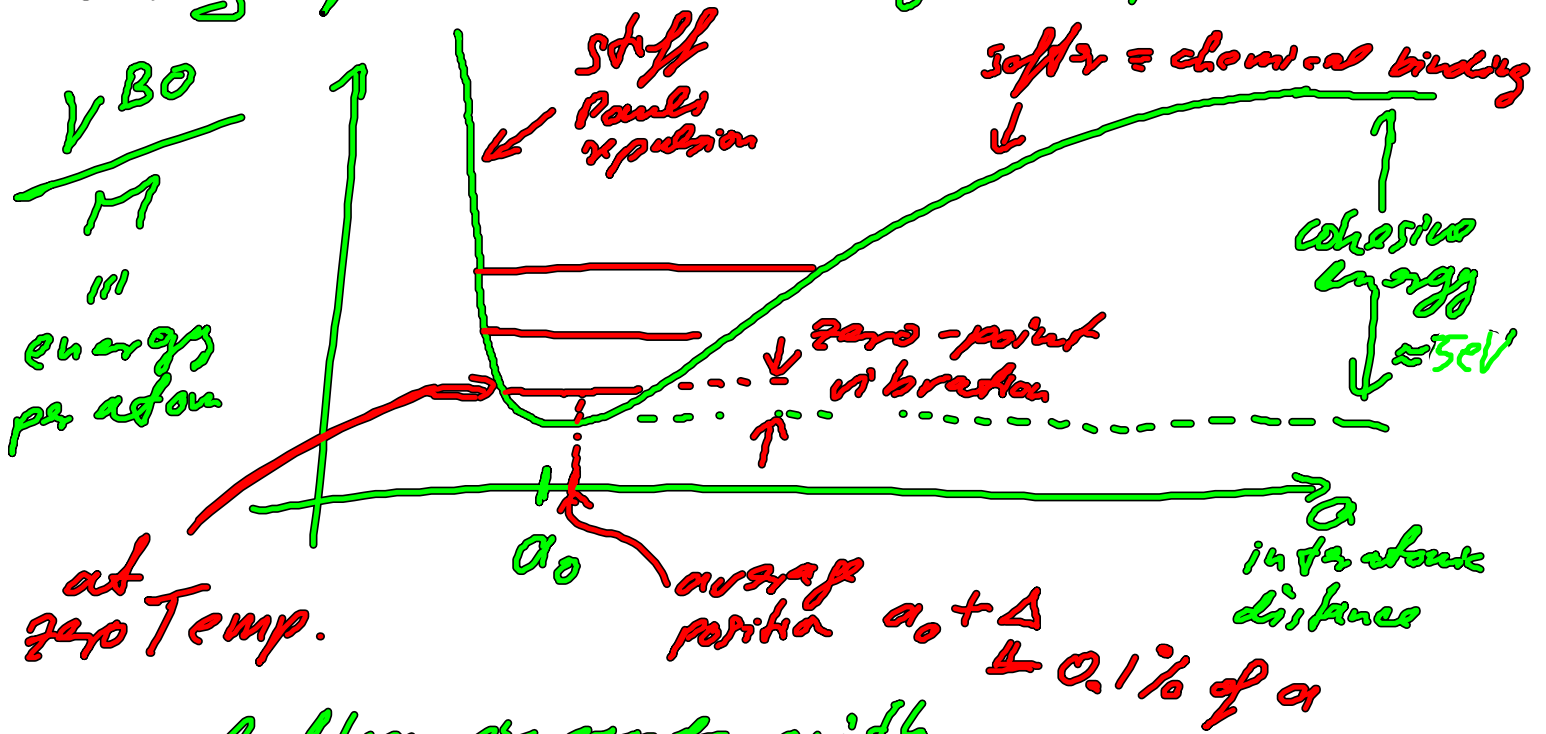
$$+ \underbrace{\langle \Delta_0 | T^{10n} | \Delta_0 \rangle}_{\text{zero-point vib.}}$$

1.2.2 An alternative route to
 analyse e-vib. coupling = "static approx."
 → exercise

1.2.3 Examples

(What is it good for?)

density-functional gives $E_0(\{\vec{R}_I\})$



⇒ lattice expands with increasing temperature

bulk modulus

$$B_0 = \frac{1}{K} = V \frac{\partial^2 V^{BO}(V)}{\partial V^2} \Big|_{a=a_0}$$

''' compressibility

2.1. Statistical Mechanics

$T = 0K$ the system is in its ground state:
 E_0^e, ϕ_0

$T > 0K$ all ϕ_ν, E_ν^e will be excited
with a certain probability:
 $\propto \exp(-E_\nu^e/k_B T)$

The ensemble is described by the
density operator $\rho = \sum P(E_\nu^e, T) |\phi_\nu\rangle \langle \phi_\nu|$

with $\sum_\nu P(E_\nu^e, T) = 1$

$$= \frac{1}{Z^e} \sum_\nu \exp(-E_\nu^e/k_B T)$$

$Z^e \equiv$ partition function

$$Z^e = \sum_\nu \exp(-E_\nu^e/k_B T) = \text{Tr} \exp(-H^e/k_B T)$$

$$-k_B T \ln Z^e = F^e = U^e - T S^e$$

" free energy internal energy entropy

$$U^e(T) = \sum_\nu E_\nu^e(T) \cdot P(E_\nu^e, T)$$

$$\left. \frac{\partial u}{\partial T} \right|_V = \left. \frac{\partial s}{\partial T} \right|_V \cdot \frac{1}{T}$$

$$u = \frac{U}{V}, \quad s = \frac{S}{V}$$

$$s^e = -k_B \sum_i \left[f(\epsilon_i, T) \ln f(\epsilon_i, T) + (1 - f(\epsilon_i, T)) \ln (1 - f(\epsilon_i, T)) \right]$$

with

$f(\epsilon_i, T) \equiv$ Fermi function

$$c_V = \frac{1}{V} \left(\frac{\partial u}{\partial T} \right)_V = \frac{T}{V} \left(\frac{\partial s}{\partial T} \right)_V$$

2.2. Fermi Statistics

