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1.1. The many-body hamiltonian

$$H\Psi = E\Psi ; \quad \Psi = \Psi\left(\{\vec{R}_I\}, \{\vec{r}_k \sigma_k\}\right)$$

positions of all nuclei

positions & spins of all electrons

1) kinetic energy of the electrons

$$T^e = \sum_{k=1}^{N} \frac{p_k^2}{2m} \qquad \vec{p}_k = \frac{\hbar}{i} \vec{\nabla}_{\vec{r}_k}$$

2) $$T^{ion} = \sum_{I=1}^{M} \frac{P_I^2}{2M_I} \qquad \vec{P}_I = \frac{\hbar}{i} \vec{\nabla}_{\vec{R}_I}$$

3) electron-electron interaction

$$V^{e-e}\left(\{\vec{r}_k \sigma_k\}\right) \approx \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{\substack{k,k' \\ k \neq k'}}^{N,N} \frac{e^2}{|\vec{r}_k - \vec{r}_{k'}|}$$

here no spin/magnetism

4) ion-ion

$$V^{ion-ion}\left(\{\vec{R}_I\}\right) = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{\substack{I,J \\ I \neq J}}^{M,M} \frac{e^2 Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}$$

also here neglecting nuclear spin. ≡ no problem

5) electron - ion

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

$= v(\vec{r}_k)$

$v(\vec{r}_k)$ = 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}

$M_{H}/m = 1,840$

$M_{Si}/m = 25,760$

$M_{Ag}/m = 86,480$

⇒ 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: $H^e = T^e + V^{e\text{-}ion} + V^{e\text{-}e}$

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

$H^e(\{\vec{R}_I\})\ \phi_\nu(\{\vec{R}_I\};\{\vec{r}_{\alpha i}, \sigma_{\alpha i}\}) = E^e_\nu\ \phi_\nu$

if $\frac{M_I}{m} \to \infty$ then H^e describes the system

we use ϕ_ν as basis set.

$$\Psi = \sum_\nu \Lambda_\nu(\{\vec{R}_I\})\ \phi_\nu(\{\vec{R}_I\},\{\vec{r}_{\alpha i}\sigma_{\alpha i}\})$$

$$H\Psi = (H^e + T^{ion} + V^{ion})\Psi = \sum_\nu \Lambda_\nu E^e_\nu \phi_\nu$$

$$+ \Lambda_\nu \phi_\nu V^{ion} + T^{ion}(\Lambda_\nu \phi_\nu)\Big]$$

$$\nabla^2_{\vec{R}_I}(\Lambda_\nu \phi_\nu) = \Big(\nabla^2_{\vec{R}_I} \Lambda_\nu\Big)\cdot \phi_\nu + \Lambda_\nu \left(\nabla^2_{R_I} \phi_\nu\right) + 2\left(\vec{\nabla}_{R_I} \Lambda_\nu\right)\left(\vec{\nabla}_{R_I} \phi_\nu\right)\Big]$$

Chain rule

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

$$\left(T^{ion} + E^e_\mu + V^{ion-ion}\right)\Lambda_\mu + \sum_\nu \sum_{I=1}^{M} -\frac{\hbar^2}{2M_I}\Big[\langle \phi_\mu | \nabla^2_{\vec{R}_I} | \phi_\nu \rangle \Lambda_\nu + 2\langle \phi_\mu | \vec{\nabla}_{R_I} | \phi_\nu \rangle \left(\vec{\nabla}_{R_I} \Lambda_\nu\right)\Big]$$

still exact

$\longmapsto$ ≡ 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,
John-Teller, Peierls distortion,
Kohn - anomaly etc.

BO approx ≡ these terms are zero
||
adiabatic
approx

$$\left(T^{ion} + V^{ion-ion} + E^e_\mu\right) \Lambda_\mu = E_\mu \Lambda_\mu$$

for $\mu = 0$: $V^{ion-ion} + E^e_\mu \equiv V^{BO}$

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

$\Lambda_\mu(\{\vec{R}_I\})$ ≡ strongly peaked
at positions of nuclei

in principle (T^{ion} ...) Λ_μ should be solved q.m. Doing so shows classical (Newton) treatment gives the result ... except for H even deuterium is nearly classical.

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

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

ground state = lowest energy state

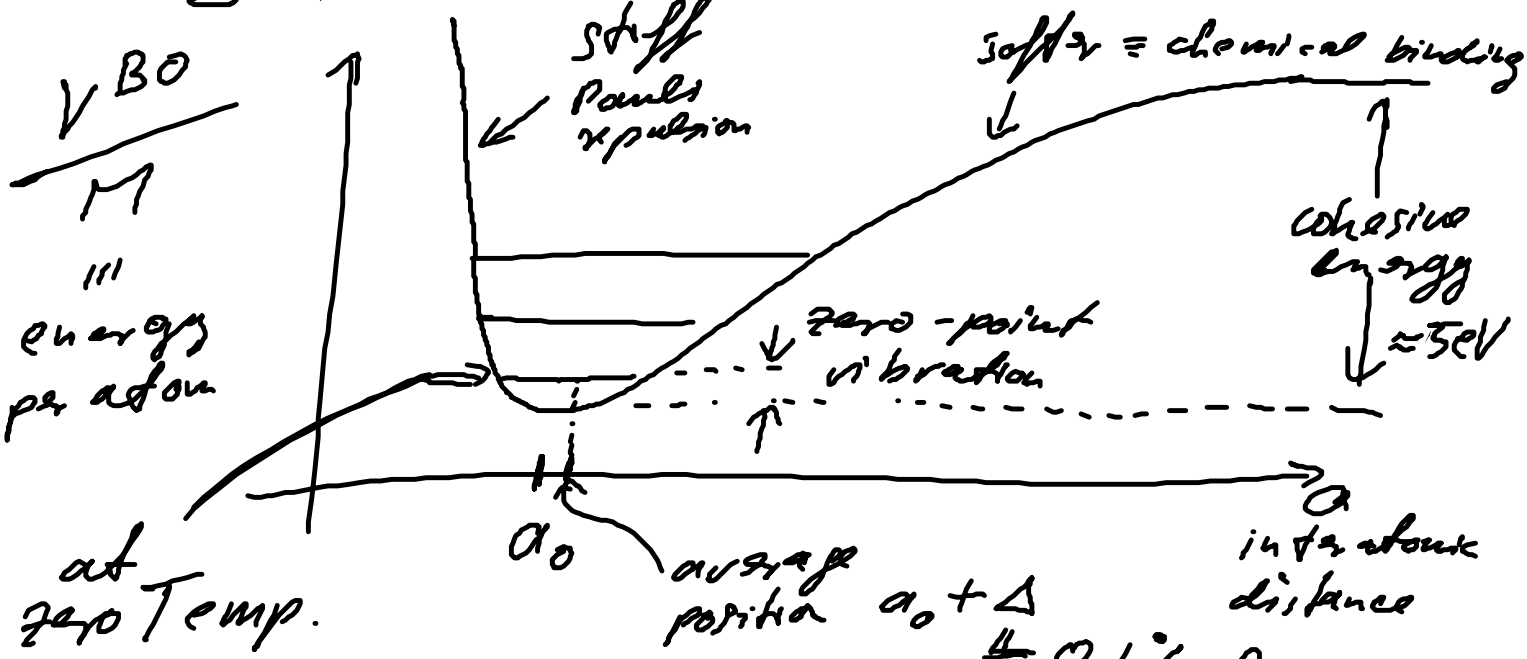
$$E = E_0^e(\{\vec{R}_I\}) + \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum \frac{e^2 Z_{v_I} Z_{v_J}}{|\vec{R}_I - \vec{R}_J|} + \underbrace{\langle \Lambda_0 | T^{ion} | \Lambda_0 \rangle}_{\text{zero-point vib.}}$$

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 $E_0^e(\{\vec{R}_I\})$



$\Rightarrow$ lattice expands with increasing temperature

bulk modulus

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

III compressibility

2.1. Statistical Mechanics

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

$T > 0K$ all ϕ_v, E_v^e will be excited with a certain probability: $\sim \exp(-E_v^e / k_B T)$

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

with $\sum_v P(E_v^e, T) = 1$

$$= \frac{1}{Z^e} \sum_v \exp(-E_v^e / k_B T)$$

$Z^e \equiv$ partion function

$$Z^e = \sum_v \exp(-E_v^e / k_B T) = Tr \exp(-H^e / k_B T)$$

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

"free energy" ← internal energy, entropy

$$\boxed{U^e(T) = \sum_v E_v^e(T) \cdot P(E_v^e, T)}$$

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

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

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

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