The self-consistent electron-nuclear dynamics in solids

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In the study of electronic structure of crystals we consider the nuclei fixed in their equilibrium positions. Now we'll discuss some consequences of the fact that the masses of nuclei, although much larger than the electron mass, are still finite.

This will enable us to establish the link between the electronic properties and the lattice dynamics, two traditional subjects of solid state physics.

The total Hamiltonian for a system of electrons and nuclei in a solid can be written as

$$H_{TOT} = H_N + H_e + H_{e-N}$$

$$\boxed{e_o^2 \equiv \frac{e^2}{4\pi\varepsilon_o}}$$

$$H_N = \sum_I \frac{P_I^2}{2M} + \frac{1}{2}\sum_{I \neq J} \frac{(ze_o)^2}{|\vec{R}_I - \vec{R}_J|}$$

$$H_e = \sum_i \frac{P_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} \frac{e_o^2}{|\vec{r}_i - \vec{r}_j|}$$

$$H_{e-N} = -\sum_{i,I} \frac{ze_o^2}{|\vec{R}_I - \vec{r}_i|}$$

** NOTE :
for simplicity of notation we assume that all the nuclei have the same charge and mass

This is an extremely complicated Hamiltonian and some approximations are inevitable.
The starting one is suggested by the large difference in the masses of nuclei and electrons.

$$\frac{m}{M} \ll 1 \implies$$ We fix the positions of the nuclei and study the electron dynamics in the static potential of the localized nuclei.

This is the <u>adiabatic</u> or the Born-Oppenheimer (BO) approximation. In this approximation, the nuclear kinetic energy (T_N) is thus neglected $(T_N \approx 0)$.

Within the BO approximation the electron dynamics is described by the <u>effective "adiabatic"</u> <u>Hamiltonian</u> :

$$H_{BO}(\vec{r};\vec{R}) = -\frac{\hbar^2}{2m}\sum_i \frac{\partial^2}{\partial \vec{r_i}^2} + \frac{e_o^2}{2}\sum_{i \neq j}\frac{1}{|\vec{r_i}-\vec{r_j}|}$$
$$-\sum_{i,I}\frac{z e_o^2}{|\vec{R_I}-\vec{r_i}|} + \frac{(Z e_o)^2}{2}\sum_{I \neq J}\frac{1}{|\vec{R_I}-\vec{R_J}|}$$

here we introduced abbreviated notation :

$$\vec{r} \equiv (\vec{r_1},...,\vec{r_N}) \longrightarrow \text{coordinates of all the electrons}$$
$$\vec{R} \equiv (\vec{R_1},...,\vec{R_M}) \longrightarrow \text{coordinates of all the nuclei}$$

The Hamiltonian H_{BO} _depends parametrically_ on the positions of nuclei.

$$H_{BO} \equiv H_{BO} \left(\vec{r} ; \vec{R} \right)$$

quantum-mechanical dynamical observables

parameters !

The electronic (band-structure) problem can then be in principle solved (and the total energy of the system determined) for all possible choices of the positions of nuclei.

We then reinstore the finite nuclear mass, i.e., we describe the motion of nuclei in accordance with the Hamiltonian

$$H = -\frac{\hbar^2}{2M} \sum_I \frac{\partial^2}{\partial \vec{R}_I^2} + E_{TOT} \left(\vec{R} \right).$$

Here $E_{TOT}(\vec{R})$ is the total (ground-state) energy of the $\bar{e}$ system, thought of as a function of nuclear coordinates. This function plays the role of _the potential energy for nuclear motion_ and defines the _adiabatic potential-energy surface._

Note that $E_{TOT}(\vec{R})$ contains not only the original Coulomb interaction between the nuclei, but also an additional contribution due to the electron motion !

In the classical approximation, which turns out to be extremely accurate, the nuclear motion is described by

$$M \ddot{\vec{R}}_I = \vec{F}_I(\vec{R}) \, ,$$

where the force $\vec{F}_I$ is given by the negative gradient of the potential-energy surface:

$$\vec{F}_I = - \frac{\partial E_{TOT}(\vec{R})}{\partial \vec{R}_I} \, .$$

But we also know that $E_{TOT}(\vec{R})$ is an eigenvalue (the smallest, to be more precise!) of H_{BO}:

$$E_{TOT}(\vec{R}) = \langle \Psi(\vec{r};\vec{R}) | H_{BO} | \Psi(\vec{r};\vec{R}) \rangle$$

where $|\Psi(\vec{r};\vec{R})\rangle$ is an eigenfuction.

Remember that in <u>Blatt 0</u> there was a problem about the <u>Hellman-Feynman</u> theorem, applicable to an arbitrary parametric Hamiltonian. Using this theorem

$$\frac{\partial E_{TOT}(\vec{R})}{\partial \vec{R}_I} = \left\langle \Psi(\vec{r};\vec{R}) \left| \frac{\partial H_{BO}}{\partial \vec{R}_I} \right| \Psi(\vec{r};\vec{R}) \right\rangle,$$

that is,

$$\boxed{\vec{F}_I = -\left\langle \Psi(\vec{r};\vec{R}) \left| \frac{\partial H_{BO}}{\partial \vec{R}_I} \right| \Psi(\vec{r};\vec{R}) \right\rangle}$$

By making use of the concrete form of H_{BO} we then obtain:

$$\vec{F}_I = \left\langle \Psi(\vec{r};\vec{R}) \left| \frac{\partial}{\partial \vec{R}_I} \left(\sum_i \frac{Z_\bullet e_0^2}{|\vec{R}_I - \vec{r}_i|} \right) \right| \Psi(\vec{r};\vec{R}) \right\rangle$$

$$- \left\langle \Psi(\vec{r};\vec{R}) \left| \frac{\partial}{\partial \vec{R}_I} \left(\sum_{J \neq I} \frac{(Z e_0^2}{|\vec{R}_I - \vec{R}_J|} \right) \right| \Psi(\vec{r};\vec{R}) \right\rangle$$

doesn't depend on electronic coordinates $\vec{r}$!

The first term can be conveniently transformed:

$$\left\langle \Psi(\vec{r};\vec{R}) \left| \frac{\partial}{\partial \vec{R}_I} \left(\sum_i \frac{Z_\bullet e^2}{|\vec{R}_I - \vec{r}_i|} \right) \right| \Psi(\vec{r};\vec{R}) \right\rangle =$$

$$= \left\langle \Psi(\vec{r};\vec{R}) \left| \frac{\partial}{\partial \vec{R}_I} \left(\sum_i \int \frac{Z e_0^2}{|\vec{R}_I - \vec{r}'|} \delta^{(3)}(\vec{r}' - \vec{r}_i)\, d^3\vec{r}' \right) \right| \Psi(\vec{r};\vec{R}) \right\rangle =$$

$$= \int \left\langle \Psi(\vec{r};\vec{R}) \left| \sum_{i=1}^N \delta^{(3)}(\vec{r}' - \vec{r}_i) \right| \Psi(\vec{r};\vec{R}) \right\rangle \frac{\partial}{\partial \vec{R}_I}\left(\frac{Z e_0^2}{|\vec{R}_I - \vec{r}'|} \right) d^3\vec{r}'$$

Now we note that

$$\langle \psi(\vec{r};\vec{R}) | \sum_{i=1}^{N} \delta^{(3)}(\vec{r}\,' - \vec{r}_i) | \psi(\vec{r};\vec{R}) \rangle = n(\vec{r}\,';\vec{R})$$

that is the total electron density at position $\vec{r}\,'$!

The last observation allows us to write the first term in the expression for $\vec{F}_I$ as :

$$\langle \psi(\vec{r};\vec{R}) | \frac{\partial}{\partial \vec{R}_I} \left(\sum_i \frac{Z e_0^2}{|\vec{r}_i - \vec{R}_I|} \right) | \psi(\vec{r};\vec{R}) \rangle$$

$$= \int d^3\vec{r}\; n(\vec{r};\vec{R}) \frac{\partial}{\partial \vec{R}_I} \left(\frac{Z e_0^2}{|\vec{R}_I - \vec{r}|} \right)$$

note that $\vec{r}$ is here just an integration variable (replaces $\vec{r}\,'$ in the above formulae) !

one should not confuse it with the collective electronic coordinate in $|\psi(\vec{r};\vec{R})\rangle$!

thus $\vec{F}_I$ can finally be written as :

$$\vec{F}_I = \int d^3\vec{r}\; n(\vec{r};\vec{R}) \frac{\partial}{\partial \vec{R}_I} \left(\frac{Z e_0^2}{|\vec{R}_I - \vec{r}|} \right)$$
$$- \frac{\partial}{\partial \vec{R}_I} \left(\sum_{J \neq I} \frac{(Z e_0)^2}{|\vec{R}_I - \vec{R}_J|} \right)$$

Thus we see that the expression for the force on a nucleus consists of two contributions : the second term is the one due to the original Coulomb interaction of the given nucleus to the other nuclei ; the first one describes the contribution of the electron motion to the nuclear dynamics !

In reality the electron-nuclear dynamics is studied self-consistently : the relaxation of the nuclear positions (starting from some assumed initial positions) is done simultaneously with the relaxation of electronic wave-functions. This is the essence of the Car-Parrinello method, which, by combining density-functional theory (DFT) approach to electronic properties with the molecular-dynamics approach to the nuclear motion, allows us to reach with unprecedented accuracy the equilibrium configurations of polynuclear systems (not only SOLIDS, but also molecules, clusters, etc.)

Important reference : R. Car and M. Parrinello, "Unified Approach for Molecular Dynamics and Density Functional Theory" Phys. Rev. Lett. 55, 2471 (1985)