

From the Schroedinger Equation to Molecular Dynamics (remarks on the notion of molecular structure)

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DIPARTIMENTO DI FISICA



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- Problems of Reductionism and the search for fundamental dofs.
(e.g. free-electron model of metal conductivity)
- P.W.Anderson opened the season of “complexity” in 1972
(P.W. Anderson, *More is different*. Science, **177**, 393-396 (1972)).

In a nutshell:

- THERE IS NO FUNDAMENTAL SCALE
- AT EACH SCALE THERE IS NEW PHYSICS
- EACH SCALE HAS ITS OWN LEVEL OF COMPREHENSION

MOLECULAR STRUCTURE

An intrinsically classical notion

- Mechanical equilibrium configurations
- No net force condition (what is a force in QM?)
- Minima of the potential energy landscape

The “fundamental” law at atomic scale

$$i\hbar \frac{\partial \tilde{\Psi}(r, R, t)}{\partial t} = \mathcal{H} \tilde{\Psi}(r, R, t) \Leftrightarrow \mathcal{H} \Psi_n = E_n \Psi_n$$

Non relativistic time dependent Schroedinger Equation with the “matter hamiltonian”:

$$\mathcal{H}(r, R; p, P) = K_N(P) + \underbrace{K_e(p) + V(r, R)}_{H_e(r, p|R)}$$

Electronic hamiltonian

Born-Oppenheimer approximation

Nuclear masses exceed electronic ones by 2-3 orders of magnitude: $m_N \gg m_e$

$$H_e(r, p | R) \Phi_s(r | R) = E_s(R) \Phi_s(r | R)$$

We split the molecular Schr. Equation into two: electronic and nuclear

Electronic wave-functions are more delocalized

$$|\nabla_R \Phi_s| \ll |\nabla_r \Phi_s|$$

$$\Psi(r, R; t) = \sum_s \chi_s(R; t) \Phi_s(r | R) \simeq \chi_0(R; t) \Phi_0(r | R)$$

adiabatic approximation: B. O. 1927

The evolution of the nuclear approximated w.f. $\chi_0(R; t)$ is given by:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} \chi_0(R; t) &= \mathcal{H}_N(R, P) \chi_0(R; t) \\ &\equiv [K_N(P) + E_0(R)] \chi_0(R; t) \end{aligned}$$

The dynamics of the nuclei, apparently independent from the electrons, is driven by $E_0(R)$ as the interaction potential (a mean field, modelizable, no more Coulomb!); the ground state electronic function parametrized by R .

In the rigid adiabatic approx. no excited electronic states, jumps are considered.

The force fields of protein MD come from models of E_0

If nuclei are heavy enough and/or temperature is high enough so that the thermal quantum length is negligible w.r. to nuclear separations:

$$\Lambda = \frac{h}{\sqrt{m_N k_B T}} \ll \text{internuclear } r$$

Then the dynamics is no more quantum, but
Newton: and nuclei move classically in the
effective potential built up by electronic glue

$$m_N \ddot{R} = -\nabla E_0(R)$$

◆ a classical system of *quantum* particles interacting via an effective interaction potential,

is be obtained ab initio, from quantum mechanics, (AIMD) by some suitable fitting procedure → *phenomenological* model, e.g. with a Pairwise Additive Potential,

◆ if PAP, the equations of motion are numerically integrable for a number of particles finite but large enough to study, by statistical approach, the thermal properties of matter

Equilibrium (classical) Statistical Mechanics (1)

a closed system evolving in time under time-independent forces will reach a STATIONARY state

the microscopic properties are ‘irrelevant’ while the statistical (or macroscopic) are stable and interesting (THERMODYNAMICS).

They can be computed by time or ensemble averages:

Equilibrium (classical) Statistical Mechanics (2)

$$O = \overline{\hat{O}(R, P)} \equiv \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt \hat{O}^{\text{micro}}(R(t), P(t)) \quad (1)$$

Temporal average of an observable along a trajectory generated by the newtonian dynamics

$$\simeq \lim_{\mathcal{N} \rightarrow \infty} \frac{1}{\mathcal{N}} \sum_{i=1}^{\mathcal{N}} \hat{O}(R(ih), P(ih)) \quad (2)$$

Estimator of (1)

↙ Relative probability of state l

$$= \lim_{\mathcal{N} \rightarrow \infty} \sum_{\ell \in \text{visited states}} \left[\frac{n_\ell}{\mathcal{N}} \right] \hat{O}_\ell \quad (3)$$

Estimator of (1) as an expected value over a probability scheme attached to “states”, to be considered as statistically independent bunches of snapshots, similar to **meso-states**

$$\simeq \int dR dP \rho(R, P) \hat{O}(R, P) = \langle \hat{O}(R, P) \rangle \quad (4)$$

Ensemble average as in MC: (1) and (4) are the same if the dynamics is ergodic

I. THE BORN-OPPENHEIMER APPROXIMATION

The next few lectures will treat the problem of quantum chemistry, a subfield of quantum mechanics also known as molecular quantum mechanics. The idea of quantum chemistry is to use only the simple facts molecules and, indeed, all of ordinary matter, can be viewed as composed only of positively charged nuclei and negatively charged electrons. This *universal* description is then subject to a quantum mechanical treatment from which the properties of the system are derived or computed.

We begin our discussion of AIMD by considering a system of N nuclei described by coordinates, $\mathbf{R}_1, \dots, \mathbf{R}_N \equiv \mathbf{R}$, momenta, $\mathbf{P}_1, \dots, \mathbf{P}_N \equiv \mathbf{P}$, and masses M_1, \dots, M_N , and N_e electrons described by coordinates, $\mathbf{r}_1, \dots, \mathbf{r}_{N_e} \equiv \mathbf{r}$, momenta, $\mathbf{p}_1, \dots, \mathbf{p}_{N_e} \equiv \mathbf{p}$, and spin variables, $s_1, \dots, s_{N_e} \equiv s$. The Hamiltonian of the system is given by

$$\begin{aligned} H &= \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\mathbf{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} \\ &\equiv T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R}) \end{aligned}$$

where m is the mass of the electron, and $Z_I e$ is the charge on the I th nucleus. In the second line, T_N , T_e , V_{ee} , V_{NN} , and V_{eN} represent the nuclear and electron kinetic energy operators and electron-electron, electron-nuclear, and nuclear-nuclear interaction potential operators, respectively. Note that this Hamiltonian is universal in that it describes all of everyday matter from biological macromolecules such as proteins, enzymes and nucleic acids, to metals and semiconductors to synthetic materials such as plastics. Thus, if we could solve for the eigenvalues and eigenfunctions of this Hamiltonian, we could, predict any property we wished of a given system. This fact lead the

$$[T_{\text{N}} + T_{\text{e}} + V_{\text{ee}}(\mathbf{r}) + V_{\text{NN}}(\mathbf{R}) + V_{\text{eN}}(\mathbf{r}, \mathbf{R})] \Psi(\mathbf{x}, \mathbf{R}) = E \Psi(\mathbf{x}, \mathbf{R})$$

Molecular eigen-value problem

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi(\mathbf{x}, \mathbf{R}) \chi(\mathbf{R})$$

Separation of scales, adiabatic factorization... $\nabla_I \chi(\mathbf{R}) \gg \nabla_I \phi(\mathbf{x}, \mathbf{R})$

$$\frac{[T_{\text{e}} + V_{\text{ee}}(\mathbf{r}) + V_{\text{eN}}(\mathbf{r}, \mathbf{R})] \phi(\mathbf{x}, \mathbf{R})}{\phi(\mathbf{x}, \mathbf{R})} = E - \frac{[T_{\text{N}} + V_{\text{NN}}(\mathbf{R})] \chi(\mathbf{R})}{\chi(\mathbf{R})}$$

$$[T_{\text{e}} + V_{\text{ee}}(\mathbf{r}) + V_{\text{eN}}(\mathbf{r}, \mathbf{R})] \phi(\mathbf{x}, \mathbf{R}) = \varepsilon(\mathbf{R}) \phi(\mathbf{x}, \mathbf{R}) \quad \text{Electronic eq}$$

$$[T_{\text{N}} + V_{\text{NN}}(\mathbf{R}) + \varepsilon_n(\mathbf{R})] \chi(\mathbf{R}) = E \chi(\mathbf{R}) \quad \text{nuclear}$$

Moreover, each electronic eigenvalue, $\varepsilon_n(\mathbf{R})$, will give rise to an electronic *surface*, and these surfaces are known as *Born-Oppenheimer surfaces*. Thus, the full internuclear potential for each electronic surface is given by $V_{\text{NN}}(\mathbf{R}) + \varepsilon_n(\mathbf{R})$. On each Born-Oppenheimer surface, the nuclear eigenvalue problem can be solved, which yields a set of levels

Nuclear motions are ruled by the time dependent Schroedinger Eq.

$$[T_N + V_{NN}(\mathbf{R}) + \varepsilon_n(\mathbf{R})] X(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} X(\mathbf{R}, t)$$

$$[T_e + V_{ee}(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R})] \phi_0(\mathbf{x}, \mathbf{R}) = \varepsilon_0(\mathbf{R}) \phi_0(\mathbf{x}, \mathbf{R})$$

$$[T_N + \varepsilon_0(\mathbf{R}) + V_{NN}(\mathbf{R})] X(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} X(\mathbf{R}, t)$$

Coupling the nuclear dynamics with electronic on the flight solutio of the electronic eigen-value problem is
Ab-Initio Car-Parrinello MD

Moreover, if nuclear quantum effects can be neglected, then we may arrive at classical nuclear evolution by assuming $X(\mathbf{R}, t)$ is of the form

$$X(\mathbf{R}, t) = A(\mathbf{R}, t)e^{iS(\mathbf{R}, t)/\hbar} \quad (11)$$

and neglecting all terms involving \hbar , which yields an approximate equation for $S(\mathbf{R}, t)$:

$$H_N(\nabla_1 S, \dots, \nabla_N S, \mathbf{R}_1, \dots, \mathbf{R}_N) + \frac{\partial S}{\partial t} = 0 \quad (12)$$

which is just the classical Hamiltonian-Jacobi equation with

$$H_N(\mathbf{P}_1, \dots, \mathbf{P}_N, \mathbf{R}_1, \dots, \mathbf{R}_N) = \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I} + V_{NN}(\mathbf{R}) + \varepsilon_0(\mathbf{R}) \quad (13)$$

denoting the classical nuclear Hamiltonian. The Hamilton-Jacobi equation is equivalent to classical motion on the ground-state surface, $E_0(\mathbf{R}) = \varepsilon_0(\mathbf{R}) + V_{NN}(\mathbf{R})$ given by

$$\begin{aligned} \dot{\mathbf{R}}_I &= \frac{\mathbf{P}_I}{M_I} \\ \dot{\mathbf{P}}_I &= -\nabla_I E_0(\mathbf{R}) \end{aligned} \quad (14)$$

Note that the force $-\nabla_I E_0(\mathbf{R})$ contains a term from the nuclear-nuclear repulsion and a term from the derivative of the electronic eigenvalue, $\varepsilon_0(\mathbf{R})$. Because of the Hellman-Feynman theorem, the latter can be expressed as

$$\nabla_I \varepsilon_0(\mathbf{R}) = \langle \phi_0(\mathbf{R}) | \nabla_I H_e(\mathbf{R}) | \phi_0(\mathbf{R}) \rangle$$

II. PROOF OF THE HELLMAN-FEYNMAN THEOREM

Consider a system with a Hamiltonian $H(\lambda)$ that depends on some parameters λ . Let $|\psi(\lambda)\rangle$ be an eigenvector of $H(\lambda)$ with eigenvalue $E(\lambda)$

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \quad (16)$$

We further assume that $|\psi(\lambda)\rangle$ is normalized so that

$$\langle\psi(\lambda)|\psi(\lambda)\rangle = 1 \quad (17)$$

The Hellman-Feynman theorem states that

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle \quad (18)$$

The proof of the Hellman-Feynman theorem is straightforward. We begin with the fact that

$$E(\lambda) = \langle\psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle \quad (19)$$

Differentiating both sides yields

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + \left\langle \frac{d\psi}{d\lambda} | H(\lambda) | \psi(\lambda) \right\rangle + \left\langle \psi | H(\lambda) | \frac{d\psi}{d\lambda} \right\rangle \quad (20)$$

Since $|\psi(\lambda)\rangle$ is an eigenvector of $H(\lambda)$, this can be written as

$$\begin{aligned} \frac{dE}{d\lambda} &= \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + E(\lambda) \left\langle \frac{d\psi}{d\lambda} | \psi(\lambda) \right\rangle + E(\lambda) \left\langle \psi | \frac{d\psi}{d\lambda} \right\rangle \\ &= \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle + E(\lambda) \left[\left\langle \frac{d\psi}{d\lambda} | \psi(\lambda) \right\rangle + \left\langle \psi | \frac{d\psi}{d\lambda} \right\rangle \right] \end{aligned}$$

However, since $|\psi(\lambda)\rangle$ is normalized, we have, from the normalization condition:

$$\begin{aligned} \langle\psi(\lambda)|\psi(\lambda)\rangle &= 1 \\ \left\langle \frac{d\psi}{d\lambda} | \psi(\lambda) \right\rangle + \left\langle \psi | \frac{d\psi}{d\lambda} \right\rangle &= 0 \end{aligned}$$

Hence, the term in square brackets vanishes, and we have

$$\frac{dE}{d\lambda} = \left\langle \psi(\lambda) \left| \frac{dH}{d\lambda} \right| \psi(\lambda) \right\rangle \quad (21)$$

which is just the Hellman-Feynman theorem.

So, we have grounded the notion of molecular structure and molecular dynamics on quantum mechanics. Moreover, we have given, through Hellmann-Feynman's theorem a meaning to the notion of Molecular forces. **E scusate se è poco**

