TDDFT and nuclear motion

We start with some general considerations. We have N_e electrons and N_n nuclei with coordinates

$$\underline{r} = (\vec{r}_1, \ldots, \vec{r}_{N_e}) \quad , \quad \underline{R} = (\vec{R}_1, \ldots, \vec{R}_{N_n})$$

The N_n nuclei have masses M_α and charges Z_α.
$\alpha \in \{1, \ldots, N_n\}$

The general form of a molecular Hamiltonian is then:

$$\hat{H}(t) = \hat{T}_n + \hat{T}_e + \hat{W}_{nn} + \hat{W}_{ne} + \hat{W}_{ee} + \hat{V}_{ext,e}(t) + \hat{V}_{ext,n}(t) \tag{1}$$

The kinetic energy for nuclei $\hat{T}_n$ and electrons $\hat{T}_e$ are given by

$$\hat{T}_n = -\sum_{\alpha=1}^{N_n} \frac{1}{2M_\alpha} \nabla^2_{R_\alpha} \qquad \hat{T}_e = -\sum_{i=1}^{N_e} \frac{1}{2} \nabla_i^2 \tag{2}$$

The various interactions $\hat{W}_{nn}$, $\hat{W}_{ne}$, and $\hat{W}_{ee}$ are given by:

$$\hat{W}_{nn} = \frac{1}{2} \sum_{\alpha \neq \beta}^{N_n} \frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|} \tag{3}$$

$$\hat{W}_{en} = -\sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} \tag{4}$$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \tag{5}$$

Then finally there is the possibility to add external fields, such as a laser pulse, acting on electrons ($\hat{V}_{ext,e}$) or nuclei ($\hat{V}_{ext,n}$):

$$\hat{V}_{ext,e}(t) = \sum_{i=1}^{N_e} v_{ext,e}(\vec{r}_i, t)$$

$$\hat{V}_{ext,n}(t) = \sum_{q=1}^{N_n} \vec{v}_{ext,n}(\vec{R}_q, t) \qquad (6)$$

for example, a dipole field:

$$v_{ext,e}(\vec{r}, t) = \vec{r} \cdot \vec{E}(t)$$

$$\vec{v}_{ext,n}(\vec{R}_q, t) = -Z_q \vec{R}_q \cdot \vec{E}(t)$$

where $\vec{E}(t)$ is a time-dependent electric field

Having defined the molecular Hamiltonian, the task is to solve the time-dependent Schrödinger equation:

$$i \partial_t \underline{\Psi}(\underline{r}, \underline{R}, t) = \hat{H}(t) \underline{\Psi}(\underline{r}, \underline{R}, t) \qquad (7)$$

$$\underline{\Psi}(\underline{r}, \underline{R}, t_0) = \underline{\Psi}(\underline{r}, \underline{R})$$

This is a high-dimensional many-body problem so it would be favourable to devise a TDDFT formalism that would reduce this problem to one-particle equations. We will later come back to this issue and first discuss a simplification based on so-called Ehrenfest dynamics.

We start by a small intermezzo on the time-dependent action principle.

Equations of motion from an action principle

Consider a collection of N_n classical particles with mass M_α and position $\bar{R}_\alpha(t)$, subject to some potential $V(\bar{R}_1, \ldots, \bar{R}_{N_n})$. Then Newton's equations for their motion is given by

$$M_\alpha \ddot{\bar{R}}_\alpha(t) = -\frac{\partial V}{\partial \bar{R}_\alpha}(\bar{R}_1, \ldots, \bar{R}_{N_n})\Big|_{\bar{R}_\gamma = \bar{R}_\gamma(t)} \qquad (8)$$

These equations can also be derived from a variational principle. We define the action functional

$$A[\underline{R}] = \int_{t_0}^{t_1} dt \left(\frac{1}{2} \sum_{\alpha=1}^{N_n} M_\alpha \dot{\bar{R}}_\alpha^2 - V(\underline{R}) \right) \qquad (9)$$

where $\underline{R} = (\bar{R}_1(t), \ldots, \bar{R}_{N_n}(t))$

Let us change $\underline{R} \to \underline{R} + \epsilon \underline{S}$

$$\underline{S} = (\bar{S}_1(t), \ldots, \bar{S}_{N_n}(t))$$

with some time-dependent functions $\bar{S}_i(t)$.

Then

$$A[\underline{R} + \epsilon \underline{S}] - A[\underline{R}]$$

$$= \int_{t_0}^{t} dt \left[\left(\sum_{\alpha=1}^{N_n} \frac{1}{2} M_\alpha (\dot{\bar{R}}_\alpha + \epsilon \dot{\bar{S}}_\alpha)^2 - V(\underline{R} + \epsilon \underline{S}) \right) - \left(\sum_{\alpha} \frac{1}{2} M_\alpha \dot{\bar{R}}_\alpha^2 - V(\underline{R}) \right) \right]$$

$$\Rightarrow \quad A[\underline{R} + \epsilon \underline{S}] - A[\underline{R}]$$

$$= \epsilon \int_{t_0}^{t_1} dt \left(\sum_{\alpha=1}^{N_n} M_\alpha \dot{\vec{R}}_\alpha \cdot \dot{\vec{S}}_\alpha - \sum_{\alpha=1}^{N_n} \frac{\partial V}{\partial \vec{R}_\alpha}(\underline{R}) \cdot \vec{S}_\alpha \right) + O(\epsilon^2)$$

$$= \epsilon \int_{t_0}^{t_1} dt \left(- \sum_{\alpha=1}^{N_n} M_\alpha \ddot{\vec{R}}_\alpha - \sum_{\alpha=1}^{N_n} \frac{\partial V}{\partial \vec{R}_\alpha}(\underline{R}) \right) \cdot \vec{S}_\alpha + \epsilon \left[\sum_{\alpha=1}^{N_n} M_\alpha \dot{\vec{R}}_\alpha \cdot \vec{S}_\alpha \right]_{t_0}^{t_1} + O(\epsilon^2)$$

where in the last step we performed at partial integration. Now suppose that $\underline{S}(t_0) = \underline{S}(t_1) = 0$, then the boundary terms cancel and we have

$$\lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[A(\underline{R} + \epsilon \underline{S}) - A(\underline{R}) \right]$$

$$= - \int_{t_0}^{t_1} dt \sum_{\alpha=1}^{N_n} \left(M_\alpha \ddot{\vec{R}}_\alpha + \frac{\partial V}{\partial \vec{R}_\alpha}(\underline{R}) \right) \cdot \vec{S}_\alpha(t) \qquad (10)$$

If $\vec{S}_\alpha(t)$ can be chosen arbitrarily (apart from $\underline{S}(t_0) = \underline{S}(t_1) = 0$) then we see that

$$0 = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[A(\underline{R} + \epsilon \underline{S}) - A(\underline{R}) \right] \qquad (11)$$

is equivalent to

$$M_\alpha \ddot{\vec{R}}_\alpha + \frac{\partial V}{\partial \vec{R}_\alpha}(\underline{R}) = 0 \qquad (12)$$

which is the same as Newton's equations (8).

So the equations of motion are implied by the action principle of Eq. (11).

Now we do a similar thing for a quantum system.

We define the action functional

$$A[\psi] = \int_{t_0}^{t_1} dt \, \langle \psi(t) | \, i\partial_t - \hat{H}(t) \, | \psi(t) \rangle \tag{13}$$

where $\langle \, | \, \rangle$ is an inner product on some Hilbert space and $\psi(t)$ is a path in the Hilbert space.

Then we can consider a nearby path

$$\psi_\epsilon(t) = \psi(t) + \epsilon \Phi(t) \tag{14}$$

and we demand

$$0 = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[A[\psi + \epsilon \Phi] - A[\psi] \right] \tag{15}$$

We can calculate this to give

$$\begin{aligned} & A[\psi + \epsilon \Phi] - A[\psi] \\ &= \int_{t_0}^{t_1} dt \left[\langle \psi + \epsilon \Phi | \, i\partial_t - \hat{H}(t) \, | \psi + \epsilon \Phi \rangle - \langle \psi | \, i\partial_t - \hat{H}(t) \, | \psi \rangle \right] \\ &= \epsilon \int_{t_0}^{t_1} dt \left[\langle \Phi | \, i\partial_t - \hat{H}(t) \, | \psi \rangle + \langle \psi | \, i\partial_t - \hat{H} | \Phi \rangle \right] + O(\epsilon^2) \end{aligned}$$

So Eq. (15) becomes

$$0 = \int_{t_0}^{t_1} dt \left[\langle \Phi | \, i\partial_t - \hat{H}(t) \, | \psi \rangle + \langle \psi | \, i\partial_t - \hat{H} \, | \Phi \rangle \right] \tag{16}$$

Since this must be true for any Φ, we can also replace Φ by $i\Phi$ such that we also find

$$0 = \int_{t_0}^{t_1} dt \left[-i\langle \Phi | i\partial_t - \hat{H}(t) | \Psi \rangle + i\langle \Psi | i\partial_t - \hat{H}(t) | \Phi \rangle \right] \quad (17)$$

From (16) and (17) it follows that

$$0 = \int_{t_0}^{t_1} dt \; \langle \Phi | i\partial_t - \hat{H}(t) | \Psi \rangle \quad (18)$$

Since this equation must be true for all Φ it follows that

$$(i\partial_t - \hat{H}(t))\,\Psi(t) = 0 \quad (19)$$

Which is precisely the time-dependent Schrödinger equation

So we established

$$0 = \lim_{\epsilon \to 0} \frac{1}{\epsilon} \left[A[\Psi + \epsilon \Phi] - A[\Psi] \right]$$

for all variations Φ (20)

$$\Rightarrow \quad (i\partial_t - \hat{H}(t))\,\Psi(t) = 0$$

This shows that the action principle implies the time-dependent Schrödinger equation.

Ehrenfest dynamics

Since Eq.(1) is high-dimensional we want to simplify it. Since the nuclei are heavy particles we can try to treat them classically and assign positions $\bar{R}_\alpha(t)$ to them.

The electrons we keep fully quantum mechanical.

We expect the electronic part of the system to be described by a wavefunction $\Psi(\underline{r}, \underline{R}(t), t)$ parametrically dependent on $\underline{R}(t) = (\bar{R}_1(t), \ldots, \bar{R}_{N_n}(t))$.

A physically inspired guess for its equation is

$$i\partial_t \Psi(\underline{r}, \underline{R}(t), t) = \hat{H}_e(t)\, \Psi(\underline{r}, \underline{R}(t), t) \tag{21}$$

where

$$\hat{H}_e(t) = \hat{T}_e + \hat{W}_{ee} + \sum_{\alpha=1}^{N_n} \sum_{j=1}^{N_e} \frac{Z_\alpha}{|\bar{r}_j - \bar{R}_\alpha(t)|} + \hat{V}_{e,ext}(t) \tag{22}$$

while for the nuclear motion itself we expect

$$M_\alpha \ddot{\bar{R}}_\alpha(t) = -\frac{\partial}{\partial \bar{R}_\alpha}\left[V_{n,ext}(\bar{R}_\alpha, t) + \sum_{\beta \neq \alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|\bar{R}_\alpha(t) - \bar{R}_\beta(t)|} \right] - \sum_{\alpha=1}^{N_n} Z_\alpha \int d\bar{r}\, n(\bar{r}, t) \left(-\frac{\partial}{\partial \bar{R}_\alpha} \frac{1}{|\bar{r} - \bar{R}_\alpha(t)|} \right) \tag{23}$$

where

$$n(\bar{r}, t) = \sum_{\sigma_1 \ldots \sigma_N} N_e \int d\bar{r}_2 \ldots d\bar{r}_{N_e} \left| \Psi(\bar{r}\sigma_1, \bar{r}_2\sigma_2, \ldots, \bar{r}_{N_e}\sigma_{N_e}, t) \right|^2$$

is the electronic density. (24)

We will derive Eqs. (21–24) from an action principle.

We define

$$A[\underline{R}, \Psi] = \int_{t_0}^{t_1} dt \left[\sum_{\alpha=1}^{N_n} \frac{1}{2} M_\alpha \dot{R}_\alpha^2 - V_{n,ext}(\underline{R}, t) - \frac{1}{2} \sum_{\alpha \neq \beta}^{N_n} \frac{Z_\alpha Z_\beta}{|R_\alpha(t) - R_\beta(t)|} + \langle \Psi | i\partial_t - \hat{H}_e(\underline{r}, \underline{R}(t), t) | \Psi \rangle \right] \quad (25)$$

where $\hat{H}_e$ is the Hamiltonian in Eq. (22).

Then making the variations

$$\underline{R}(t) + \epsilon_1 \underline{S}(t), \quad \Psi \to \Psi(t) + \epsilon_2 \underline{\Phi}(t)$$

Gives

$$A[\underline{R} + \epsilon_1 \underline{S}, \Psi + \epsilon_2 \underline{\Phi}] - A[\underline{R}, \Psi]$$

$$= \epsilon_1 \int_{t_0}^{t_1} dt \left[\sum_{\alpha=1}^{N_n} M_\alpha \ddot{R}_\alpha \cdot \underline{S}_\alpha - \sum_{\alpha=1}^{N_n} \frac{\partial}{\partial R_\alpha} \left[V_{n,ext}(R_\alpha, t) + \sum_{\beta \neq \alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|R_\alpha(t) - R_\beta(t)|} \right] \cdot \hat{S}_\alpha(t) - \langle \Psi | \frac{\partial \hat{H}_e}{\partial \vec{R}_\alpha} \cdot \hat{S}_\alpha(t) | \Psi \rangle \right]$$

$$+ \epsilon_2 \int_{t_0}^{t_1} dt \left[\langle \Phi | i\partial_t - \hat{H}_e | \Psi \rangle + \langle \Psi | i\partial_t - \hat{H}_e | \Phi \rangle \right] \quad (26)$$

$$+ O(\epsilon_1^2, \epsilon_2^2, \epsilon_1 \epsilon_2)$$

Requiring the independent variations in $\underline{R}$ and Ψ to be zero then gives

$$0 = \lim_{\epsilon_1 \to 0} \frac{1}{\epsilon_1} \left[A(\underline{R} + \epsilon_1 \underline{S}, \Psi) - A(\underline{R}, \Psi) \right] = 0$$

$$0 = \lim_{\epsilon_2 \to 0} \frac{1}{\epsilon_2} \left[A(\underline{R}, \Psi + \epsilon_2 \underline{\Phi}) - A(\underline{R}, \Psi) \right] = 0 \qquad (2f)$$

then gives

$$0 = \int_{t_0}^{t_1} dt \left[-M_\alpha \ddot{\underline{R}}_\alpha - \frac{\partial}{\partial \underline{R}_\alpha} \left[V_{n,ext}(R_\alpha, t) + \sum_{\beta \neq \alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|R_\alpha(t) - R_\beta(t)|} \right] - \langle \Psi | \frac{\partial \hat{H}_e}{\partial R_\alpha} | \Psi \rangle \right] \cdot \hat{S}_\alpha(t) + \left[\sum_{\alpha=1}^{N_n} M_\alpha \dot{R}_\alpha \cdot S_\alpha \right]_{t_0}^{t_1}$$

$$0 = \int_{t_0}^{t_1} dt \left[\langle \Phi | i\partial_t - \hat{H}_e(t) | \Psi \rangle + \langle \Psi | i\partial_t - \hat{H}_e(t) | \Phi \rangle \right]$$

As before we require $\underline{S}(t_0) = \underline{S}(t_1) = 0$ and if both equations are valid for arbitrary variations S_α and Φ we obtain

$$M_\alpha \ddot{\underline{R}}_\alpha = - \frac{\partial}{\partial \underline{R}_\alpha} \left[V_{n,ext}(R_\alpha, t) + \sum_{\beta \neq \alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|R_\alpha(t) - R_\beta(t)|} \right] - \langle \Psi | \frac{\partial \hat{H}_e}{\partial R_\alpha} | \Psi \rangle \qquad (2d)$$

$$(i\partial_t - \hat{H}_e(t)) \Psi(t) = 0$$

Now

$$\langle \Psi | \frac{\partial \hat{H}_e}{\partial \underline{R}_\alpha} | \Psi \rangle = \langle \Psi | \frac{\partial \hat{W}_{en}}{\partial \underline{R}_\alpha} | \Psi \rangle \qquad (2g)$$

$$= - \sum_{\alpha=1}^{N_n} Z_\alpha \int d\underline{r}\, n(\underline{r}, t) \frac{\partial}{\partial \underline{R}_\alpha} \left(\frac{1}{|\underline{r} - \underline{R}_\alpha|} \right)$$

Inserting (2g) into (2d) gives Eq. (23).

We note that the equations we derived can also be found in:

E.K.U. Gross, J.F. Dobson, and M. Petersilka
"Density Functional theory of time-dependent phenomena"
in Topics in Current Chemistry, Vol. 181, p. 81 (1996)
(See Ch. 3 Eq. (82))

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In conclusion:

We could derive the Ehrenfest dynamics of classical nuclei and interacting quantum electrons from an action principle.

The equation of motion for the electrons is still a many-body equation. We therefore would like to simplify these equations using a TDDFT approach. So let us discuss this next.

TDDFT for Ehrenfest dynamics

The Ehrenfest equation for the electrons in Eqs. (21) and (22) is still an equation for an interacting many-body system. We can write it as

$$i\partial_t \Psi = \left[\hat{T}_e + \hat{W}_{ee} + \hat{V}_{el}(t) + \hat{V}_{e,ext}(t) \right] \Psi(t) \tag{30}$$

where we defined the potential $\hat{V}_{el}(t)$ due to classical nuclei as

$$\hat{V}_{el}(t) = \sum_{i=1}^{N_e} v_{el}(\hat{r}_i, \underline{R}(t)) \tag{31}$$

$$V_{el}(\vec{r}, \underline{R}(t)) = -\sum_{\gamma=1}^{N_n} \frac{Z_\gamma}{|\vec{r} - \vec{R}_\gamma(t)|} \tag{32}$$

We would like to replace (30) with a Kohn-Sham system. Eq. (30) is just an purely electronic system. By the (extended Runge-Gross theorem then there is a unique non-interacting system with potential $\hat{V}_s(t)$ producing the density from Eq. (30)

We have the KS-system:

$$\hat{H}_s(t) = \hat{T} + \hat{V}_s(t) \tag{33}$$

and KS-eqns.

$$\left(-\frac{1}{2}\nabla^2 + v_s([n];r,t) \right) \varphi_j(r\sigma,t) = i\partial_t \varphi_j(r\sigma,t) \tag{34}$$

$$n(\vec{r}t) = \sum_{j=1}^{N_e} \sum_{\sigma} |\varphi_j(r\sigma,t)|^2$$

For this system we can define an xc-potential by

$$V_{xc}([n];\bar{r}t) = V_s([n];\bar{r}t) - V_H([n];\bar{r}t) - V_{el}(\bar{r},\underline{R}(t)) - V_{e,ext}(\bar{r}t)$$

$$V_H([n];\bar{r}t) = \int d\bar{r}' \frac{n(\bar{r}'t)}{|\bar{r}-\bar{r}'|} \qquad (35)$$

So that the KS-eqns become

$$\left[-\frac{1}{2}\nabla^2 + V_{el}(\bar{r},\underline{R}(t)) + V_{e,ext}(\bar{r}t) + V_H([n];\bar{r}t) + V_{xc}([n];\bar{r}t)\right]\varphi_j(\bar{r}\sigma,t)$$
$$= i\partial_t \varphi_j(\bar{r}\sigma,t) \qquad (36)$$

$$n(\bar{r}t) = \sum_\sigma \sum_{j=1}^{N_e} |\varphi_j(\bar{r}\sigma,t)|^2$$

This equation needs to be complemented by Eq. (23)

$$M_\gamma \ddot{\bar{R}}_\alpha(t) = -\frac{\partial}{\partial \bar{R}_\gamma}\left[V_{n,ext}(\bar{R}_\alpha,t) + \sum_{\beta\neq\alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|\bar{R}_\alpha(t)-\bar{R}_\beta(t)|}\right]$$
$$- \int d\bar{r}\, n(\bar{r}t) \frac{\partial}{\partial \bar{R}_\gamma} V_{el}(\bar{r},\underline{R}(t)) \qquad (37)$$

Since $n(\bar{r}t)$ produces the exact density $n(\bar{r}t)$ Eq. (37) produces the identical classical nuclear dynamics of the interacting Ehrenfest dynamics.

In practice $V_{xc}([n];\bar{r}t)$ needs to be approximated, and a common choice is the adiabatic LDA (ALDA).

A final remark

The time-dependent KS-potential $v_S([n];\bar{r}t)$ is not a real-time functional derivative of some functional $A_S[n]$

Suppose

$$v_S([n];\bar{r}t) = \frac{\delta A_S[n]}{\delta n(\bar{r}t)} \qquad (38)$$

Then

$$\frac{\delta v_S(\bar{r}t)}{\delta n(\bar{r}'t')} = \frac{\delta^2 A_S}{\delta n(\bar{r}t)\delta n(\bar{r}'t')} \qquad (39)$$

We also new

$$\chi_S^{-1}(rt,r't') = \frac{\delta v_S(\bar{r}t)}{\delta n(r't')}$$

and this is a retarded function (causality)

However if A_S is twice differentiable then

$$\frac{\delta^2 A}{\delta n(rt)\delta n(r't')} = \frac{\delta^2 A}{\delta n(r't')\delta n(rt)}$$

which is in contradiction with Eq. (39)

As a consequence there is no mathematically rigorous derivation of the KS - Ehrenfest equations from an action principle.

Existing derivations neglect inconsistencies with boundary conditions that are incompatible with v-representability.

The symmetry - causality paradox mentioned can be resolved by considering an action functional on a so-called Keldysh contour but this brings us too much out of this course material.