1 Dirac–Frenkel variational principal (DFVP)

Time dependant Shrödinger equation:

$$i\hbar\frac{\partial|\Phi_{ex}\rangle}{\partial t} = \hat{H}|\Phi_{ex}\rangle \tag{1}$$

We will consider the following mean value:

$$W = \frac{\langle\Phi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Phi\rangle}{\langle\Phi|\Phi\rangle}$$

which, if calculated on exact solutions $|\Phi_{ex}\rangle$ of (1), equals to zero, and its variation: $\delta W = 0$

If $|\Phi_{ex}\rangle$ is an exact solution of (1), then the norm conservation condition is satisfied:

$$\frac{\partial\langle\Phi_{ex}|\Phi_{ex}\rangle}{\partial t} = 0$$

But we do not know beforehand about norm of arbitrary function $|\Phi\rangle$. We can consider mean value of $i\hbar\frac{\partial}{\partial t}$:

$$\langle\omega\rangle = \frac{\langle\Phi|i\hbar\frac{\partial}{\partial t}|\Phi\rangle}{\langle\Phi|\Phi\rangle}$$

Let us calculate difference between $\langle\omega\rangle$ and its complex conjugate:

$$\langle\omega\rangle - \langle\omega\rangle^* = \frac{i\hbar(\langle\Phi|\frac{\partial\Phi}{\partial t}\rangle + \langle\frac{\partial\Phi}{\partial t}|\Phi\rangle)}{\langle\Phi|\Phi\rangle}$$

$$\frac{i}{\hbar}\left(\langle\omega\rangle^* - \langle\omega\rangle\right) = \frac{\partial}{\partial t}\ln\langle\Phi|\Phi\rangle$$

Now we will solve this equation to obtain time dependance of norm:

$$N(t) = N(0)e^P,\ \text{where } P = \frac{i}{\hbar}\int_0^t \left(\langle\omega\rangle^* - \langle\omega\rangle\right)\, dt'$$

We can see, that norm conservation condition is satisfied, when $P = 0,\ \langle\omega\rangle \in \mathbb{R}$ and hence $W \in \mathbb{R}$ But if it is an approximate solution we can not guarantee conservation of norm!

But let us assume, that we can construct function $|\Phi'\rangle$, that differes from $|\Phi\rangle$ by angular multiplier:

$$|\Phi'\rangle = |\Phi\rangle \cdot e^Q,\ \text{where } Q = \frac{i}{\hbar}\int_0^t \alpha(t')\, dt',\ \alpha(t') \in \mathbb{C}$$

We need to find parameter $\alpha(t)$, so that norm $\langle\Phi'|\Phi'\rangle$ is conserved. We will consider a mean value once again:

$$\langle\omega'\rangle = \frac{\langle\Phi'|i\hbar\frac{\partial}{\partial t}|\Phi'\rangle}{\langle\Phi'|\Phi'\rangle} = \frac{\langle\Phi|e^{-Q}i\hbar\cdot\frac{i}{\hbar}\alpha(t)e^{Q} + i\hbar\frac{\partial}{\partial t}|\Phi\rangle}{\langle\Phi|\Phi\rangle} = \langle\omega\rangle - \alpha$$

If $\langle\omega'\rangle \in \mathbb{R}$, then:

$$0 = \langle\omega'\rangle - \langle\omega'\rangle^* = \langle\omega\rangle - \langle\omega\rangle^* - 2iIm(\alpha)$$

$$iIm(\alpha) = \frac{1}{2}\left(\langle\omega\rangle - \langle\omega\rangle^*\right)$$

$$\alpha = Re(\alpha) + iIm(\alpha) = Re(\alpha) + \frac{1}{2}\left(\langle\omega\rangle - \langle\omega\rangle^*\right)$$

$$\langle\omega'\rangle = \langle\omega\rangle - \alpha = \langle\omega\rangle - \frac{1}{2}\left(\langle\omega\rangle - \langle\omega\rangle^*\right) - Re(\alpha) = \frac{1}{2}\left(\langle\omega\rangle + \langle\omega\rangle^*\right) - Re(\alpha)$$

$$|\Phi'\rangle = |\Phi\rangle\cdot e^{Q} = |\Phi\rangle\cdot e^{R}\cdot e^{-0.5P},\ \text{where } R = \frac{i}{\hbar}\int_0^t Re(\alpha(t'))\,dt'$$

As $N(t) = N(0)\cdot e^{P}$, we have:

$$|\Phi'\rangle = |\Phi\rangle\cdot e^{R}\cdot\left(\frac{N(0)}{N(t)}\right)^{1/2}$$

As we've discussed previously, for an exact solution of (1) $|\Phi_{ex}\rangle$ mean value W equals to zero. Let us consider mean values W', calculated on function $|\Phi'\rangle$:

$$W' = \langle H\rangle - \langle\omega'\rangle = \langle H\rangle - \frac{1}{2}\left(\langle\omega\rangle + \langle\omega\rangle^*\right) + Re(\alpha)$$

Now we need to understand, what α should be to make W' equal to zero:

$$Re(\alpha) = -\langle H\rangle + \frac{1}{2}\left(\langle\omega\rangle + \langle\omega\rangle^*\right)$$

$$\alpha = -\langle H\rangle + \frac{1}{2}\left(\langle\omega\rangle + \langle\omega\rangle^*\right) + \frac{1}{2}\left(\langle\omega\rangle - \langle\omega\rangle^*\right) = \langle\omega\rangle - \langle H\rangle = -W$$

But if $\alpha = -W$, we will obtain:

$$|\Phi'\rangle = |\Phi\rangle\cdot e^{-\frac{i}{\hbar}\int_0^t W\,dt}$$

$$\langle\Phi'|\Phi'\rangle_t = \langle\Phi|\Phi\rangle_t\cdot e^{-\frac{i}{\hbar}\int_0^t (W-W^*)\,dt} = \langle\Phi|\Phi\rangle_0\cdot e^{P}\cdot e^{-P} = \langle\Phi|\Phi\rangle_0$$

So we have built functions $|\Phi'\rangle$, that have conserved norm and lead to zero W'.

Let us consider for simplicity function $|\Psi\rangle$ to be from the family of functions $|\Phi'\rangle$. This function has conserved norm, and mean value W, calculated on this function, is real. As the norm of $|\Psi\rangle$ doesn't change with time, we can write the following equation:

$$\delta\langle\Psi|\Psi\rangle = \langle\delta\Psi|\Psi\rangle + \langle\Psi|\delta\Psi\rangle = 0$$

We will consider only variations $|\delta\Psi\rangle$, that are orthogonal to $|\Psi\rangle$. Then:

$$\langle\delta\Psi|\Psi\rangle = 0,\ \langle\Psi|\delta\Psi\rangle = 0 \tag{2}$$

Now we can write down variation δW. For simplicity, we shall denote $\langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle$ as A and $\langle\Psi|\Psi\rangle$ as B:

$$W = \frac{A}{B},\ \delta W = \frac{B\cdot\delta A - A\cdot\delta B}{B^2} = \frac{\delta A - W\delta B}{B}$$

$$\delta A - W\delta B = \langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle + \langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\delta\Psi\rangle - W\langle\delta\Psi|\Psi\rangle - W\langle\Psi|\delta\Psi\rangle =$$

$$= \langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle + \langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\delta\Psi\rangle - W\delta\langle\Psi|\Psi\rangle$$

As $\delta\langle\Psi|\Psi\rangle = 0,\ \delta W = 0$, we obtain:

$$\langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle = 0 \text{ — Dirac–Frenkel variational principal} \tag{3}$$

$$\langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\delta\Psi\rangle = 0$$

We shall consider the second equation:

$$\langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\delta\Psi\rangle = \left\langle \left(\hat{H} - i\hbar\frac{\partial}{\partial t}\right)\Psi \middle| \delta\Psi \right\rangle - i\hbar\left\langle \frac{\partial\Psi}{\partial t} \middle| \delta\Psi \right\rangle - i\hbar\left\langle \Psi \middle| \frac{\partial}{\partial t}\delta\Psi \right\rangle =$$

$$= \langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle^* - i\hbar\frac{\partial}{\partial t}\langle\Psi|\delta\Psi\rangle = 0$$

Thus, the second equation is a mere consiquence of Dirac–Frenkel variational principal (3) and condition (2).

Previously we have discussed the case of orthogonal variation $|\delta\Psi\rangle$. Arbitraty variations $|\delta\Psi\rangle$ can be rewritten as sum of $|\Psi\rangle$ and $|\delta_\perp\Psi\rangle$:

$$|\delta\Psi\rangle = c_{||}|\Psi\rangle + c_\perp|\delta_\perp\Psi\rangle$$

Variation of W will have the following look:

$$\delta W = \langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle + \langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\delta\Psi\rangle - W\langle\delta\Psi|\Psi\rangle - W\langle\Psi|\delta\Psi\rangle =$$

$$= \langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t} - W|\Psi\rangle + \langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t} - W|\delta\Psi\rangle =$$

$$= 2Re(c_{||})\langle\Psi|\hat{H}-i\hbar\frac{\partial}{\partial t}-W|\Psi\rangle - c_{\perp}^{*}\langle\delta_{\perp}\Psi|\hat{H}-i\hbar\frac{\partial}{\partial t}-W|\Psi\rangle - c_{\perp}\langle\Psi|\hat{H}-i\hbar\frac{\partial}{\partial t}-W|\delta_{\perp}\Psi\rangle$$

The first term equals to zero, because:

$$W = \frac{\langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle}{\langle\Psi|\Psi\rangle},\ \langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t} - W|\Psi\rangle = 0$$

The last two terms are equal to zero due to Dirac–Frenkel variational principle.

We have discussed arbitrary variations of wave function $|\Psi\rangle$, that don't affect parameters of hamiltonian $\hat{H}$. To write DFVP in the most genral form, we need to consider variations $|\delta\Psi\rangle$ of the following form:

$$|\delta\Psi\rangle = |\frac{\partial\Psi}{\partial\varepsilon}\rangle\delta\epsilon,\ \hat{H} = \hat{H}(\varepsilon)$$

To preserve the form of DFVP for that kind of variation, we need to introduce one more condition, that should be met by approximate wave function $|\Psi\rangle$. Let us consider the following equation:

$$\langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle = i\hbar\langle\Phi_{ex}(t)|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle$$

where $|\Phi_{ex}(t)\rangle$ — exact solution of time dependant Shrödinger equation. That equation is a statement of time dependant Hellman–Feynman theorem (tdHFT). To prove it, we will consider the following matrix element:

$$\frac{\partial}{\partial\varepsilon}\langle\Phi_{ex}(t)|\hat{H}|\Phi_{ex}(t)\rangle = \langle\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}|\hat{H}|\Phi_{ex}(t)\rangle + \langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle + \langle\Phi_{ex}(t)|\hat{H}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle =$$

$$= i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}|\frac{\partial\Phi_{ex}(t)}{\partial t}\rangle - i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial t}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle + \langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle$$

$$\langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle = i\hbar\frac{\partial}{\partial\varepsilon}\langle\Phi_{ex}(t)|\frac{\partial\Phi_{ex}(t)}{\partial t}\rangle + i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial t}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle - i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}|\frac{\partial\Phi_{ex}(t)}{\partial t}\rangle =$$

$$= i\hbar\langle\Phi_{ex}(t)|\frac{\partial^2\Phi_{ex}(t)}{\partial\varepsilon\partial t}\rangle + i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial t}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle =$$

$$= i\hbar\frac{\partial}{\partial t}\langle\Phi_{ex}(t)|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle$$

Now we need to consider δW in terms of new type of variations:

$$\delta W = \frac{\delta A - W\delta B}{B}$$

As we remember, $\delta B = 0$. Thus, to ensure $\delta W = 0$, we need $\delta A = 0$:

$$\delta\langle\Psi|\hat{H}-i\hbar\frac{\partial}{\partial t}|\Psi\rangle = \langle\delta\Psi|\hat{H}-i\hbar\frac{\partial}{\partial t}|\Psi\rangle + \langle\delta\Psi|\hat{H}-i\hbar\frac{\partial}{\partial t}|\Psi\rangle^{*} - i\hbar\frac{\partial}{\partial t}\langle\Psi|\frac{\partial\Psi}{\partial\varepsilon}\rangle\delta\varepsilon + \langle\Psi|\frac{\partial\hat{H}}{\partial\varepsilon}|\Psi\rangle\delta\varepsilon$$

We need to make our function $|\Psi\rangle$ to behave in such a way, that tdHFT will be valid. Then we will obtain DFVP.

2 Equations of motions in DFVP formalism

Let us assume, that function $|\Psi\rangle$ can be spanned over linear combination of basis functions $\{|\phi_k(\vec{\lambda})\rangle\}_{k=1}^N$:

$$|\Psi\rangle = \sum_{k=1}^{N} C_k(t)|\phi_k(\vec{\lambda})\rangle, \dim\{\vec{\lambda}\} = M$$

Then we can consider a variation of $|\Psi\rangle$:

$$|\delta\Psi\rangle = \sum_{k=1}^{N}\left(\delta C_k|\phi_k\rangle + C_k\sum_{j=1}^{M}|\frac{\partial\phi_k}{\partial\lambda_{kj}}\rangle\delta\lambda_{kj}\right)$$

Thus, using Dirac–Frenkel variational principle, we will obtain:

$$\delta C_m^*\sum_{k=1}^{N}\langle\phi_m|\hat{H} - i\hbar\frac{\partial}{\partial t}|C_k\phi_k\rangle = 0$$

$$\delta\lambda_{mj}^*\sum_{k=0}^{N}C_m^*\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\hat{H} - i\hbar\frac{\partial}{\partial t}|C_k\phi_k\rangle = 0$$

As variations are independant and arbitrary, we will get two sets of equations:

$$\sum_{k=1}^{N}\langle\phi_m|\hat{H} - i\hbar\frac{\partial}{\partial t}|C_k\phi_k\rangle = 0$$

$$\sum_{k=0}^{N}C_m^*\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\hat{H} - i\hbar\frac{\partial}{\partial t}|C_k\phi_k\rangle = 0$$

Let us consider the first equation:

$$\sum_{k=1}^{N}C_k\langle\phi_m|\hat{H}|\phi_k\rangle - i\hbar\langle\phi_m|\phi_k\rangle\dot{C}_k - i\hbar\sum_{l=1}^{M}\langle\phi_m|\frac{\partial\phi_k}{\partial\lambda_{kl}}\rangle\dot{\lambda}_{kl} = 0$$

$$i\hbar\sum_{k=1}^{N}\mathbb{S}_{mk}\dot{C}_k = \sum_{k=1}^{N}\left(\mathbb{H}_{mk} - i\hbar\sum_{l=1}^{M}\langle\phi_m|\frac{\partial\phi_k}{\partial\lambda_{kl}}\rangle\dot{\lambda}_{kl}\right)C_k$$

$$i\hbar\mathbb{S}\dot{\vec{C}} = (\mathbb{H} - i\hbar\tau)\vec{C}$$

$$\dot{\vec{C}} = -\frac{i}{\hbar}\mathbb{S}^{-1}(\mathbb{H} - i\hbar\tau)\vec{C}$$

$$\dot{C}_k = -\frac{i}{\hbar}\sum_{n,r=1}^{N} \mathbb{S}^{-1}_{kn}(\mathbb{H}_{nr} - i\hbar\tau_{nr})C_r$$

And the second one:

$$\sum_{k=1}^{N}\left(C^*_m C_k\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\hat{H}|\phi_k\rangle - i\hbar\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\phi_k\rangle C^*_m\dot{C}_k - i\hbar\sum_{l=1}^{M} C^*_m C_k\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\frac{\partial\phi_k}{\partial\lambda_{kl}}\rangle\dot{\lambda}_{kl}\right) = 0$$

$$\sum_{k=1}^{N}\left(C^*_m C_k\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\hat{H}|\phi_k\rangle - \langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\phi_k\rangle\sum_{n,r=1}^{N}\mathbb{S}^{-1}_{kn}\mathbb{H}_{nr}C^*_m C_r\right) =$$

$$= \sum_{k=1}^{N}\left(-i\hbar\sum_{n,r=1}^{N}\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\phi_k\rangle\mathbb{S}^{-1}_{kn}\sum_{l=1}^{M}\langle\phi_n|\frac{\partial\phi_r}{\partial\lambda_{rl}}\rangle\dot{\lambda}_{rl}C^*_m C_r + i\hbar\sum_{l=1}^{M} C^*_m C_k\langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\frac{\partial\phi_k}{\partial\lambda_{kl}}\rangle\dot{\lambda}_{kl}\right)$$

$$\rho_{mk} = C^*_m C_k$$

$$\mathbb{H}^{(j0)}_{ml} = \langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\hat{H}|\phi_k\rangle$$

$$\mathbb{S}^{(j0)}_{mk} = \langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\phi_k\rangle$$

$$\mathbb{S}^{(0l)}_{nr} = \langle\phi_n|\frac{\partial\phi_r}{\partial\lambda_{rl}}\rangle$$

$$\mathbb{S}^{(jl)}_{mk} = \langle\frac{\partial\phi_m}{\partial\lambda_{mj}}|\frac{\partial\phi_k}{\partial\lambda_{kl}}\rangle$$

$$\sum_{k=1}^{N}\rho_{mk}\mathbb{H}^{(j0)}_{mk} - \sum_{r=1}^{N}\rho_{mr}\left(\sum_{k,n=1}^{N}\mathbb{S}^{(j0)}_{mk}\mathbb{S}^{-1}_{kn}\mathbb{H}_{nr}\right) =$$

$$= i\hbar\sum_{l=1}^{M}\left(\sum_{k=1}^{N}\rho_{mk}\mathbb{S}^{(jl)}_{mk}\dot{\lambda}_{kl} - \sum_{r=1}^{N}\rho_{mr}\left(\sum_{k,n=1}^{N}\mathbb{S}^{(j0)}_{mk}\mathbb{S}^{-1}_{kn}\mathbb{S}^{(0l)}_{nr}\right)\dot{\lambda}_{rl}\right)$$

$$\sum_{k=1}^{N}\rho_{mk}\left(\mathbb{H}^{(j0)}_{mk} - (\mathbb{S}^{(j0)}\mathbb{S}^{-1}\mathbb{H})_{mk}\right) = i\hbar\sum_{l=1}^{M}\sum_{k=1}^{N}\rho_{mk}\left(\mathbb{S}^{(jl)}_{mk} - (\mathbb{S}^{(j0)}\mathbb{S}^{-1}\mathbb{S}^{(0l)})_{mk}\right)\dot{\lambda}_{kl}$$

$$Y^j_m = \sum_{k=1}^{N}\rho_{mk}\left(\mathbb{H}^{(j0)}_{mk} - (\mathbb{S}^{(j0)}\mathbb{S}^{-1}\mathbb{H})_{mk}\right)$$

$$X^{jl}_{mk} = \rho_{mk}\left(\mathbb{S}^{(jl)}_{mk} - (\mathbb{S}^{(j0)}\mathbb{S}^{-1}\mathbb{S}^{(0l)})_{mk}\right)$$

$$i\hbar\dot{\Lambda} = \mathbb{X}^{-1}\mathbb{Y},\ \text{where } \Lambda \text{ is matrix}$$

Thus, we have two sets of equations:

$$\dot{\vec{C}} = -\frac{i}{\hbar}\mathbb{S}^{-1}(\mathbb{H} - i\hbar\tau)\vec{C}$$

$$\dot{\Lambda} = -\frac{i}{\hbar}\mathbb{X}^{-1}\mathbb{Y}$$

3 Gaussian wave packets

For basis functions $|\phi_k\rangle$ we can choose frozen width Gaussian wave packets (fwGWP):

$$|g_k(\vec{q}_k, \vec{p}_k)\rangle = \left(\frac{\pi}{\omega}\right)^{1/4} \exp\left(\sum_\alpha -\frac{1}{2}\omega(r_\alpha - q_{k\alpha})^2 + ip_{k\alpha}(r_\alpha - q_{k\alpha})\right)$$

where $\alpha \in \{x, y, z\}$ We can transform parameters $(\vec{q}_k, \vec{p}_k)$ to $(\vec{\xi}_k, \vec{\eta}_k)$:

$$\xi_{k\alpha} = \omega q_{k\alpha} + ip_{k\alpha}$$

$$\eta_{k\alpha} = \frac{1}{4}\left(\ln\left[\frac{\omega}{\pi}\right] - 2\omega q_{k\alpha}^2\right) - iq_{k\alpha}p_{k\alpha}$$

Thus we will obtain another representation of GWP:

$$|g_k(\vec{\xi}_k, \vec{\eta}_k)\rangle = \exp\left(\sum_\alpha -\frac{1}{2}\omega r_\alpha^2 + \xi_{k\alpha}r_\alpha + \eta_{k\alpha}\right)$$

The matrix elements, that we need to use in EOM:

$$\mathbb{S}_{mk} = \exp\left(\sum_\alpha \frac{(\xi_{m\alpha}^* + \xi_{k\alpha})^2}{4\omega} + (\eta_{m\alpha}^* + \eta_{k\alpha})\right)$$