

1 Dirac–Frenkel variational principal (DFVP)

Time dependant Shrödinger equation:

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

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

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

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

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

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

We see, that if function has a conserved norm, then $P = 0$, $\langle \omega \rangle \in \mathbb{R}$ 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 differs 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. Once again, we will consider a mean value:

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

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

$$0 = \langle \omega' \rangle - \langle \omega' \rangle^* = \langle \omega \rangle - \langle \omega \rangle^* - 2i \text{Im}(\alpha)$$

$$i \text{Im}(\alpha) = \frac{1}{2} (\langle \omega \rangle - \langle \omega \rangle^*)$$

$$\alpha = \text{Re}(\alpha) + i \text{Im}(\alpha) = \text{Re}(\alpha) + \frac{1}{2} (\langle \omega \rangle - \langle \omega \rangle^*)$$

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

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

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

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

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

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

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

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:

$$\langle\delta\Psi|\Psi\rangle = 0, \quad \langle\Psi|\delta\Psi\rangle = 0 \quad (2)$$

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 :

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

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

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

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

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

We shall consider the second equation:

$$\begin{aligned} \langle\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\delta\Psi\rangle &= \left\langle \left(\hat{H} - i\hbar\frac{\partial}{\partial t} \right) \Psi \middle| \delta\Psi \right\rangle - i\hbar \left\langle \frac{\partial\Psi}{\partial t} \middle| \delta\Psi \right\rangle - i\hbar \left\langle \Psi \middle| \frac{\partial}{\partial t} \delta\Psi \right\rangle = \\ &= \langle\delta\Psi|\hat{H} - i\hbar\frac{\partial}{\partial t}|\Psi\rangle^* - i\hbar\frac{\partial}{\partial t}\langle\Psi|\delta\Psi\rangle = 0 \end{aligned}$$

Thus, the second equation is a mere consequence 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:

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

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

The first term equals zero, because:

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

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:

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

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:

$$\begin{aligned} \frac{\partial}{\partial\varepsilon}\langle\Phi_{ex}(t)|\hat{H}|\Phi_{ex}(t)\rangle &= \langle\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}|\hat{H}|\Phi_{ex}(t)\rangle + \langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle + \langle\Phi_{ex}(t)|\hat{H}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle = \\ &= i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}|\frac{\partial\Phi_{ex}(t)}{\partial t}\rangle - i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial t}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle + \langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle \\ \langle\Phi_{ex}(t)|\frac{\partial\hat{H}}{\partial\varepsilon}|\Phi_{ex}(t)\rangle &= i\hbar\frac{\partial}{\partial\varepsilon}\langle\Phi_{ex}(t)|\frac{\partial\Phi_{ex}(t)}{\partial t}\rangle + i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial t}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle - i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}|\frac{\partial\Phi_{ex}(t)}{\partial t}\rangle = \\ &= i\hbar\langle\Phi_{ex}(t)|\frac{\partial^2\Phi_{ex}(t)}{\partial\varepsilon\partial t}\rangle + i\hbar\langle\frac{\partial\Phi_{ex}(t)}{\partial t}|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle = \\ &= i\hbar\frac{\partial}{\partial t}\langle\Phi_{ex}(t)|\frac{\partial\Phi_{ex}(t)}{\partial\varepsilon}\rangle \end{aligned}$$

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 make our function $|\Psi\rangle$ to behave in such a way, that *tdHFT* is still 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 $\{|\phi_k(\vec{\lambda})\rangle\}_{k=1}^N$:

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

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

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

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

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

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

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

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

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

Let us consider the first equation:

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

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

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

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

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

And the second one:

$$\begin{aligned} \sum_{k=1}^N \left(C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \hat{H} \middle| \phi_k \right\rangle - i\hbar \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \phi_k \right\rangle C_m^* \dot{C}_k - i\hbar \sum_{l=1}^M C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} \right) &= 0 \\ \sum_{k=1}^N \left(C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \hat{H} \middle| \phi_k \right\rangle - \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \phi_k \right\rangle \sum_{n,r=1}^N \mathbb{S}_{kn}^{-1} \mathbb{H}_{nr} C_m^* C_r \right) &= \\ = \sum_{k=1}^N \left(-i\hbar \sum_{n,r=1}^N \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \phi_k \right\rangle \mathbb{S}_{kn}^{-1} \sum_{l=1}^M \left\langle \phi_n \middle| \frac{\partial \phi_r}{\partial \lambda_{rl}} \right\rangle \dot{\lambda}_{rl} C_m^* C_r + i\hbar \sum_{l=1}^M C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} \right) \end{aligned}$$

$$\rho_{mk} = C_m^* C_k$$

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

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

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

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

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

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

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

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

Thus, we have two sets of equations:

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

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