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 met:

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

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 dependence 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 met, 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 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. 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) $|\Phi_{ex}\rangle$ W mean value equals 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 makes W' 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 $|\Psi\rangle$ of 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 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:

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

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

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

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

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

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

We shall consider the second equation:

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

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

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 as follows look:

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

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

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

$$+c_{\perp} \left\langle \Psi \left| \hat{H} - i\hbar\frac{\partial}{\partial t} - W \right| \delta_{\perp}\Psi \right\rangle$$

The first term equals zero, because

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

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 Dirac–Frenkel variational principle in the most general form, we need to consider variations $|\delta\Psi\rangle$ of the following form:

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

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:

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

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

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

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

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

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

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

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

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

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 $\delta A = 0$:

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

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

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 represented by basis functions $\{|\phi_k(\lambda_1, \ldots, \lambda_M)\rangle\}_{k=1}^{N}$ expansion:

$$|\Psi\rangle = \sum_{k=1}^{N} C_k(t) |\phi_k(\lambda_1, \ldots, \lambda_M)\rangle$$

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

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

Thus, using Dirac–Frenkel variational principle we will obtain

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

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

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

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

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

Let us consider the first equation:

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

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

$$i\hbar \sum_{k=1}^{N} \mathbb{S}_{mk} \dot{C}_k = \sum_{k=1}^{N} (\mathbb{H}_{mk} - i\hbar \boldsymbol{\tau}_{mk}) C_k$$

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

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

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

And the second one:

$$\sum_{k=1}^{N} \left(C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \hat{H} \middle| \phi_k \right\rangle - i\hbar \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \phi_k \right\rangle C_m^* \dot{C}_k - \right.$$

$$\left. - i\hbar \sum_{l=1}^{M} C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} \right) = 0$$

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

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

$$\left. + i\hbar \sum_{l=1}^{M} C_m^* C_k \left\langle \frac{\partial \phi_m}{\partial \lambda_{mj}} \middle| \frac{\partial \phi_k}{\partial \lambda_{kl}} \right\rangle \dot{\lambda}_{kl} \right)$$

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

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

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

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

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

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

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

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

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

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

$$i\hbar \sum_{l=1}^{M} \sum_{k=1}^{N} \mathbb{X}^{(jl)}_{mk} \dot{\lambda}_{kl} = \mathbb{Y}^{j}_{m}$$

$$i\hbar \mathbb{X} \dot{\Lambda} = \mathbb{Y}$$

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

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):

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

where ω — time independent parameter, that can be set equal to width of zeroth eigenfunction of harmonic oscillator. We can transform parameters $(\vec{\xi}_k, \vec{\eta}_k)$ to $(\vec{q}_k, \vec{p}_k)$:

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

where $\vec{q}_k$ — center of gaussian wave packets, $\vec{p}_k$ — momentum of wave packet. We can assume, that wave packet, centered in phase space at $(\vec{q}_k, \vec{p}_k)$, represents particle at the same point of phase space. In this representation gaussian wave packet looks like:

$$|g_k(\vec{q}_k, \vec{p}_k)\rangle = \left(\frac{\pi}{\omega}\right)^{-3/4} \exp\left(\frac{1}{\hbar}\sum_{\alpha=x,y,z}\left[-\frac{1}{2}\omega(r_\alpha - q_{k\alpha})^2 + i p_{k\alpha}(r_\alpha - q_{k\alpha})\right]\right) = g_{kx} g_{ky} g_{kz}$$

The trick of GWP basis is as follows: we generate basis, using grid in phase space, then switch from parameters $(\vec{q}_k, \vec{p}_k)$ to $(\vec{\xi}_k, \vec{\eta}_k)$, where we can easily calculate matrix elements for equations of motion (see below). But then we understand, that actually we do not need to propagate both ξ_k and η_k, rather we can calculate only $\dot{\xi}_k$, switch back to $\dot{q}_k = Re(\dot{\xi}_k)/\omega$ and $\dot{p}_k = Im(\dot{\xi}_k)$ and calculate $q_k(t + \Delta t)$ and $p_k(t + \Delta t)$.

The matrix elements, that we need to use in equations of motions ($\hbar = 1$):

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

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

$$\mathbb{S}_{mk}^{(\alpha 0)} = \left\langle \frac{\partial g_m}{\partial \xi_{m\alpha}}\middle| g_k \right\rangle = \langle g_{m\alpha}|r_\alpha|g_{k\alpha}\rangle \left(\prod_{\beta\neq\alpha}\mathbb{S}_{mk,\beta}\right) = \frac{(\xi_{m\alpha}^* + \xi_{k\alpha})}{2\omega}\mathbb{S}_{mk,x}\mathbb{S}_{mk,y}\mathbb{S}_{mk,z}$$

$$\mathbb{S}_{mk}^{(0\alpha)} = \left\langle g_m \middle| \frac{\partial g_k}{\partial \xi_{k\alpha}} \right\rangle = \langle g_{m\alpha}|r_\alpha|g_{k\alpha}\rangle \left(\prod_{\beta\neq\alpha}\mathbb{S}_{mk,\beta}\right) = \frac{(\xi_{m\alpha}^* + \xi_{k\alpha})}{2\omega}\mathbb{S}_{mk,x}\mathbb{S}_{mk,y}\mathbb{S}_{mk,z}$$

$$\mathbb{S}_{mk}^{(\alpha\beta)} = \left\langle \frac{\partial g_m}{\partial \xi_{m\alpha}} \middle| \frac{\partial g_k}{\partial \xi_{k\beta}} \right\rangle = \langle g_{m\alpha}|r_\alpha|g_{k\alpha}\rangle\langle g_{m\beta}|r_\beta|g_{k\beta}\rangle \mathbb{S}_{mk,\gamma} =$$
$$= \frac{(\xi_{m\alpha}^* + \xi_{k\alpha})(\xi_{m\beta}^* + \xi_{k\beta})}{4\omega^2}\mathbb{S}_{mk,x}\mathbb{S}_{mk,y}\mathbb{S}_{mk,z}$$

$$\mathbb{S}_{mk}^{(\alpha\alpha)} = \langle g_{k\alpha}|r_\alpha^2|g_{m\alpha}\rangle\left(\prod_{\beta\neq\alpha}\mathbb{S}_{mk,\beta}\right) = \left(\frac{(\xi_{m\alpha}^* + \xi_{k\alpha})^2}{4\omega^2} + \frac{1}{2\omega}\right)\mathbb{S}_{mk,x}\mathbb{S}_{mk,y}\mathbb{S}_{mk,z}$$

$$\mathbb{H}_{mk} = \langle g_m|\hat{H}|g_k\rangle = \langle g_m|\hat{T}_N|g_k\rangle + \langle g_m|V(\vec{r})|g_k\rangle =$$

$$= \frac{\$_{mk,x}\$_{mk,y}\$_{mk,z}}{M} \sum_{\alpha} \left(\frac{1}{2}\left(\omega - \xi_{k\alpha}^2\right) + \xi_{k\alpha}\frac{(\xi_{m\alpha}^* + \xi_{k\alpha})}{2} - \left(\frac{(\xi_{m\alpha}^* + \xi_{k\alpha})^2}{8} + \frac{\omega}{4} \right) \right) +$$

$$+\langle g_m|V(\vec{r})|g_k\rangle =$$

$$= \frac{\$_{mk,x}\$_{mk,y}\$_{mk,z}}{M} \sum_{\alpha} \left(\frac{\omega + 2\xi_{m\alpha}^*\xi_{k\alpha}}{4} - \frac{(\xi_{m\alpha}^* + \xi_{k\alpha})^2}{8} \right) + \langle g_m|V(\vec{r})|g_k\rangle =$$

$$= \frac{\$_{mk,x}\$_{mk,y}\$_{mk,z}}{M} \sum_{\alpha} \left(\frac{2\omega - (\xi_{m\alpha}^* - \xi_{k\alpha})^2}{8} \right) + \langle g_m|V(\vec{r})|g_k\rangle$$

$$\mathbb{H}_{mk}^{(\alpha 0)} = \left\langle \frac{\partial g_m}{\partial \xi_{m\alpha}} \middle| \hat{H} \middle| g_k \right\rangle = -\frac{1}{M}\sum_{\beta} \left\langle g_m \middle| r_\alpha \frac{\partial^2}{\partial \beta^2} \middle| g_k \right\rangle + \langle g_m|V(\vec{r})|g_k\rangle =$$

$$= -\frac{1}{M}\left\langle g_{m\alpha} \middle| r_\alpha \frac{\partial^2}{\partial \alpha^2} \middle| g_{k\alpha} \right\rangle \left(\prod_{\beta\neq\alpha} \$_{mk,\beta} \right) + \langle g_m|V(\vec{r})|g_k\rangle +$$

$$+ \frac{\$_{mk,x}\$_{mk,y}\$_{mk,z}}{M} \frac{\xi_{m\alpha}^* + \xi_{k\alpha}}{2\omega} \sum_{\beta\neq\alpha} \left(\frac{2\omega - (\xi_{m\beta}^* - \xi_{k\beta})^2}{8} \right) =$$

$$= \frac{\$_{mk,x}\$_{mk,y}\$_{mk,z}}{M} \frac{\xi_{m\alpha}^* + \xi_{k\alpha}}{2\omega} \sum_{\beta} \left(\frac{2\omega - (\xi_{m\beta}^* - \xi_{k\beta})^2}{8} \right) + \langle g_m|V(\vec{r})|g_k\rangle$$

For all matrix elements, except for the mean value of electron potential, we have obtained explicit equations. For mean value of potential energy we need potential energy surface. We can use harmonic decomposition (analytical equations) or numerical techniques (Gaussian quadratures) to calculate $\langle g_m|V(\vec{r})|g_k\rangle$.

Combining DFVP and frozen width GWP, we will obtain calculation technique called variational multi-configurational Gaussian method [1].

4 Tests

First, let's consider time dependent Hellmann–Feynman theorem, when $|\Psi\rangle = |g\rangle$ — one gaussian wave packet, $\varepsilon = \vec{q}$ or $\vec{p}$, $\hbar = 1$.

$$\left\langle g \middle| \frac{\partial \hat{H}}{\partial \vec{q}} \middle| g \right\rangle = i\frac{\partial}{\partial t}\left\langle g \middle| \frac{\partial g}{\partial \vec{q}} \right\rangle$$

$$\left| \frac{\partial g}{\partial \vec{q}} \right\rangle = (\omega(\vec{r} - \vec{q}) - i\vec{p})|g\rangle$$

$$\left\langle g \middle| \frac{\partial g}{\partial \vec{q}} \right\rangle = \omega\langle g|\vec{r}|g\rangle - \vec{\xi}\langle g|g\rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{q}} \right. \right\rangle = \left(\frac{\vec{\xi}^* + \vec{\xi}}{2} - \vec{\xi} \right) \langle g|g \rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{q}} \right. \right\rangle = \left(\frac{\vec{\xi}^* - \vec{\xi}}{2} \right) \langle g|g \rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{q}} \right. \right\rangle = \left(\frac{\vec{\xi}^* - \vec{\xi}}{2} \right) \langle g|g \rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{q}} \right. \right\rangle = -i\vec{p}\langle g|g \rangle$$

$$\left\langle g \left| \frac{\partial \hat{H}}{\partial \vec{q}} \right| g \right\rangle = \frac{\partial}{\partial t} \left(\vec{p}\langle g|g \rangle \right)$$

As norm is conserved, we will obtain:

$$\dot{\vec{p}} = \frac{\left\langle g \left| \frac{\partial \hat{H}}{\partial \vec{q}} \right| g \right\rangle}{\langle g|g \rangle}$$

For parameter $\vec{p}$:

$$\left\langle g \left| \frac{\partial \hat{H}}{\partial \vec{p}} \right| g \right\rangle = i\frac{\partial}{\partial t} \left\langle g \left| \frac{\partial g}{\partial \vec{p}} \right. \right\rangle$$

$$\left| \frac{\partial g}{\partial \vec{p}} \right\rangle = i(\vec{r} - \vec{q})|g\rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{p}} \right. \right\rangle = i\langle g|(\vec{r} - \vec{q})|g\rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{p}} \right. \right\rangle = i\langle g|\vec{r}|g\rangle - i\vec{q}\langle g|g\rangle$$

$$\left\langle g \left| \frac{\partial g}{\partial \vec{p}} \right. \right\rangle = 0$$

$$\left\langle g \left| \frac{\partial \hat{H}}{\partial \vec{p}} \right| g \right\rangle = 0$$

Let us consider Hellmann–Feynman equation with repsect to time as ε:

$$\left\langle g \left| \frac{\partial \hat{H}}{\partial t} \right| g \right\rangle = i\frac{\partial}{\partial t} \left\langle g \left| \frac{\partial g}{\partial t} \right. \right\rangle$$

The left side is equal to zero, the right side:

$$\left\langle g \left| \frac{\partial g}{\partial t} \right. \right\rangle = \left\langle g \left| \frac{\partial g}{\partial \vec{q}} \right. \right\rangle \dot{\vec{q}} + \left\langle g \left| \frac{\partial g}{\partial \vec{p}} \right. \right\rangle \dot{\vec{p}} =$$

$$= -i\vec{p}\dot{\vec{q}}\langle g|g\rangle$$

$$\frac{\partial \vec{p}\dot{\vec{q}}}{\partial t}\langle g|g\rangle = 0$$

$$\frac{\partial \vec{p}\dot{\vec{q}}}{\partial t} = 0$$

Список литературы

[1] G.W. Richings, I. Polyak, K.E. Spinlove, G.A. Worth, I. Burghardt, and B. Lasorne. Quantum dynamics simulations using gaussian wavepackets: the vmcg method. *International Reviews in Physical Chemistry*, 34(2):269–308, 2015.