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:

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

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

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

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:

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

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

Thus, the second equation is a mere 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:

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

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

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

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

The first term equals to 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 DFVP in the most genral form, we need to consider variations $|\delta\Psi\rangle$ of the following form:

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

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:

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

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

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

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

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

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

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

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

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

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 spanned over linear combination of basis functions $\{|\phi_k(\lambda_1, \ldots, \lambda_M)\rangle\}_{k=1}^N$:

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

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 independant 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:

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

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

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

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

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

And the second one:

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

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

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

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

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

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

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

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

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

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

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

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

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

$$Y^{l}_{k} = \sum_{r=1}^{N} \rho_{kr} \left(\mathbb{H}^{(j0)}_{kr} - (\mathbb{S}^{(l0)} \mathbb{S}^{-1} \mathbb{H})_{kr} \right)$$

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

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

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):

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

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

$$\xi_{k\alpha} = \omega q_{k\alpha} + i p_{k\alpha}$$

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

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:

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

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

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

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

$$\mathbb{S}_{mk}^{(\alpha\beta)} = \left\langle \frac{\partial g_m}{\partial \xi_{m\alpha}} \middle| \frac{\partial g_k}{\partial \xi_{k\beta}} \right\rangle = \langle g_{m\alpha}|r_\alpha|g_{k\alpha}\rangle\langle g_{m\beta}|r_\beta|g_{k\beta}\rangle \mathbb{S}_{mk,\gamma} =$$

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

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

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

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

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

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

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

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

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

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

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

For all matrix elements, except the mean value of electron potential, we have obtained explicit equations.

The trick of GWP representation is as follows: we shift from parameters (q_k, p_k) to (ξ_k, η_k), where we can more easily calculate matrix elements. But then we also see, that actually we do not need to propogate both ξ_k and η_k. Rather we can calculate $\dot{\xi}_k$, 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 $p_k(t + \Delta t)$.

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

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.