# Кар-Паринело

# Молекулна динамика

The total ground–state energy of the interacting system of electrons with classical nuclei fixed at positions $\{\mathbf{R}_I\}$ can be obtained

$$\min_{\Psi_0} \{ \langle \Psi_0 | \mathcal{H}_{\rm e} | \Psi_0 \rangle \} \;=\; \min_{\{\phi_i\}} E^{\rm KS}[\{\phi_i\}]$$

$$\begin{aligned} E^{\rm KS}[\{\phi_i\}] \;&=\; T_{\rm s}[\{\phi_i\}] + \int d\mathbf{r}\;\; V_{\rm ext}(\mathbf{r})\; n(\mathbf{r}) \\ &\quad + \frac{1}{2} \int d\mathbf{r}\;\; V_{\rm H}(\mathbf{r})\; n(\mathbf{r}) + E_{\rm xc}[n] + E_{\rm ions}(\mathbf{R}^N) \end{aligned}$$

$\{\phi_i(\mathbf{r})\}$ Kohn–Sham orbitals

$$\langle \phi_i \mid \phi_j \rangle = \delta_{ij} \qquad\qquad n(\mathbf{r}) \;=\; \sum_i^{\rm occ} f_i \mid \phi_i(\mathbf{r}) \mid^2$$

$$T_{\mathrm{s}}[\{\phi_i\}] = \sum_{i}^{\mathrm{occ}} f_i \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle$$

Кинетична енергия на невзаимодействащи си атоми

$V_{\mathrm{ext}}(\mathbf{r})$ Външен потенциал

$$V_{\mathrm{H}}(\mathbf{r}) = \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\,\mathbf{r}-\mathbf{r}'\,|}$$

Потенциал на Хартри

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi n(\mathbf{r})$$

$E_{\mathrm{xc}}[n]$ Обменно-корелационен функционал

$$\left\{-\frac{1}{2}\nabla^2 + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}\right\}\phi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\phi_j(\mathbf{r})$$

$$\left\{-\frac{1}{2}\nabla^2 + V^{\rm KS}(\mathbf{r})\right\}\phi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\phi_j(\mathbf{r})$$

$$H^{\rm KS}\phi_i(\mathbf{r}) = \sum_j \Lambda_{ij}\phi_j(\mathbf{r})$$

$$\frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} = V_{\rm xc}(\mathbf{r})$$

Чрез унитарно преобразование уравнението може да се приведе в канонична форма

$$H^{\rm KS}\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$\frac{\delta E^{\rm KS}}{\delta\phi_i^\star(\mathbf{r})} = f_i H_{\rm e}^{\rm KS}\phi_i(\mathbf{r})$$

Сили действащи на орбиталите

# Борн-Опенхаймер молекулна динамика

$$\mathcal{L}_{\mathrm{BO}}(\mathbf{R}^N, \dot{\mathbf{R}}^N) = \sum_{I=1}^{N} \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 - \min_{\{\phi_i\}} E^{\mathrm{KS}}[\{\phi_i\}; \mathbf{R}^N]$$

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I \left[ \min_{\{\phi_i\}} E^{\mathrm{KS}}[\{\phi_i\}; \mathbf{R}^N] \right]$$

Сили действаши на ядрата $\frac{d}{d\mathbf{R}_I}\left[\min_{\{\phi_i\}} E^{\mathrm{KS}}[\{\phi_i\};\mathbf{R}^N]\right]$

$$\mathcal{E}^{\mathrm{KS}} = E^{\mathrm{KS}} + \sum_{ii} \Lambda_{ij}\left(\langle\phi_i \mid \phi_j\rangle - \delta_{ij}\right)$$

$$\begin{aligned}\frac{d\mathcal{E}^{\mathrm{KS}}}{d\mathbf{R}_I} &= \frac{\partial E^{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij}\Lambda_{ij}\frac{\partial}{\partial \mathbf{R}_I}\langle\phi_i \mid \phi_j\rangle \\ &\quad + \sum_i\left[\frac{\partial E^{\mathrm{KS}}}{\partial\langle\phi_i \mid} + \sum_j \Lambda_{ij} \mid \phi_j\rangle\right]\frac{\partial\langle\phi_i \mid}{\partial \mathbf{R}_I}\end{aligned}$$

При опимизирани орбитали

$$F^{\mathrm{KS}}(\mathbf{R}_I) = -\frac{\partial E^{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij}\Lambda_{ij}\frac{\partial}{\partial \mathbf{R}_I}\langle\phi_i \mid \phi_j\rangle$$

# Кар-Паринело молекулна динамика

$$\mathcal{L}_{\mathrm{CP}}[\mathbf{R}^N, \dot{\mathbf{R}}^N, \{\Phi_i\}, \{\dot{\Phi}_i\}] = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu \left\langle \dot{\Phi}_i \middle| \dot{\Phi}_i \right\rangle - \mathcal{E}^{\mathrm{KS}} \left[ \{\Phi_i\}, \mathbf{R}^N \right]$$

Уравненията за движение

$$\frac{d}{dt} \frac{\partial \mathcal{L}_{\mathrm{CP}}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}_{\mathrm{CP}}}{\partial \mathbf{R}_I}$$

$$\frac{d}{dt} \frac{\delta \mathcal{L}_{\mathrm{CP}}}{\delta \langle \dot{\Phi}_i |} = \frac{\delta \mathcal{L}_{\mathrm{CP}}}{\delta \langle \Phi_i |}$$

$$
\begin{aligned}
M_I \ddot{\mathbf{R}}_I(t) &= -\frac{\partial E^{\mathrm{KS}}}{\partial \mathbf{R}_I} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \Phi_i \mid \Phi_j \rangle \\
\mu \ddot{\Phi}_i(t) &= -\frac{\delta E^{\mathrm{KS}}}{\delta \langle \Phi_i \mid} + \sum_{j} \Lambda_{ij} \mid \Phi_j \rangle
\end{aligned}
$$

$\mu$ Фиктивна маса

$$
E_{\mathrm{cons}} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \frac{1}{2} \mu \left\langle \dot{\Phi}_i \middle| \dot{\Phi}_i \right\rangle + E^{\mathrm{KS}} \left[ \{\Phi_i\}, \mathbf{R}^N \right]
$$

Запазваща се величина

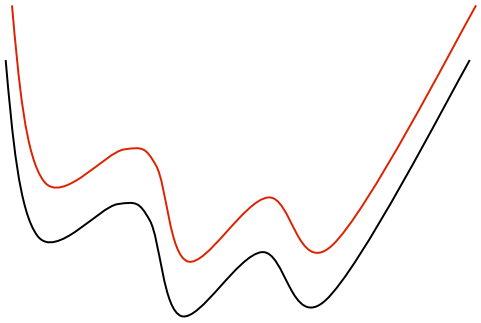
## *Моделът работи добре, ако*

$$\mu \ll M_s \rightarrow K_e \approx 0$$

***Кинетичната енергия на електроните е пренебрежима в сравнение с масите на атомите***

$$K_e + K_I + E_{pot} \approx K_I + E_{pot}$$

Пълната енергия на системата



***Състоянието на системата се пропагира адиабатно в тънък слой над потенциалната повърхнина***

***Възможности:***

- ***Големина на системата – от няколко стотици до няколко хиляди атома***
- ***Времева стъпка ~0.1 fs***
- ***Продължителност на симулацията – няколко десетки ps***

$$F(\Phi_i) = -f_i H^{\mathrm{KS}} \phi_i$$

Сили действащи на орбиталите

$$F(\mathbf{R}_I) = -\frac{\partial E^{\mathrm{KS}}}{\partial \mathbf{R}_I}$$

Сили действащи на атомните ядра

$$\begin{aligned} F_c(\Phi_i) &= \sum_j \Lambda_{ij} \mid \Phi_j \rangle \\ F_c(\mathbf{R}_I) &= \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \mathbf{R}_I} \langle \Phi_i \mid \Phi_j \rangle \end{aligned}$$

# Unit Cell and Plane Wave Basis

$$\mathbf{h} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3] \qquad \Omega = \det \mathbf{h}$$

Обем на клетката

$$\mathbf{r} = \mathbf{h}\mathbf{s}$$

Скалиране на координатите

$$\mathbf{r}_{\mathrm{pbc}} = \mathbf{r} - \mathbf{h}\left[\mathbf{h}^{-1}\mathbf{r}\right]_{\mathrm{NINT}}$$

Периодични гранични условия

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\,\delta_{ij} \qquad [\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3] = 2\pi(\mathbf{h}^{\mathrm{t}})^{-1}$$

$$f_{\mathbf{G}}^{\mathrm{PW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \exp[i\mathbf{G}\cdot\mathbf{r}] = \frac{1}{\sqrt{\Omega}} \exp[2\pi\, i\, \mathbf{g}\cdot\mathbf{s}]$$

Плоски вълни. Образуват ортонормиран базис

$$\mathbf{G} = 2\pi(\mathbf{h}^{\mathrm{t}})^{-1}\mathbf{g} \qquad \mathbf{g} = [i,j,k]$$

Периодична функция може да бъде представена по следния начин

$$\psi(\mathbf{r}) = \psi(\mathbf{r}+\mathbf{L}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \psi(\mathbf{G}) \exp[i\,\mathbf{G}\cdot\mathbf{r}]$$

$$V^{\mathrm{KS}}(\mathbf{r}) = V^{\mathrm{KS}}(\mathbf{r}+\mathbf{L})$$ Потенциал на Кон-Шан

Орбиталите могат да се представят като

$$\Phi(\mathbf{r}) = \Phi_i(\mathbf{r},\mathbf{k}) = \exp[i\,\mathbf{k}\cdot\mathbf{r}]\;\; u_i(\mathbf{r},\mathbf{k})$$

$$u_i(\mathbf{r},\mathbf{k}) = u_i(\mathbf{r}+\mathbf{L},\mathbf{k})$$

$$u_i(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} c_i(\mathbf{G},\mathbf{k})\exp[i\mathbf{G}\cdot\mathbf{r}]$$

$$\Phi_i(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{\Omega}}\sum_{\mathbf{G}} c_i(\mathbf{G},\mathbf{k})\exp[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}]$$

$$
\begin{aligned}
n(\mathbf{r}) &= \frac{1}{\Omega} \sum_i \int d\mathbf{k}\; f_i(\mathbf{k}) \sum_{\mathbf{G},\mathbf{G}'} c_i^\star(\mathbf{G}',\mathbf{k}) c_i(\mathbf{G},\mathbf{k}) \exp[i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}] \\
&= \sum_{\mathbf{G}} n(\mathbf{G}) \exp[i\,\mathbf{G}\cdot\mathbf{r}]
\end{aligned}
$$

$$
\frac{1}{2}\,|\mathbf{G}|^2 \le E_{\mathrm{cut}} \qquad\qquad N_{\mathrm{PW}} = \frac{1}{2\pi^2}\;\Omega\;E_{\mathrm{cut}}^{3/2}
$$

$E_{\mathrm{cut}}$ is in Hartree units.

# Kinetic Energy and Local Potentials

$$\frac{1}{2}\nabla^2 \, e^{i\mathbf{G}\cdot\mathbf{r}} = -\frac{1}{2} \mid \mathbf{G} \mid^2 \, e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$E_{\mathrm{kin}} = \sum_i \sum_{\mathbf{G}} \frac{1}{2} f_i \, |\mathbf{G}|^2 \, |c_i(\mathbf{G})|^2 \qquad\qquad F_{\mathrm{kin}} = \frac{1}{2} \, |\mathbf{G}|^2 \, c_i(\mathbf{G})$$

The plane waves do not depend on the atomic positions, therefore there are no Pulay forces and no contribution of the kinetic energy to the forces on the nuclei.

$$\int d\mathbf{r}' \; V(\mathbf{r}, \mathbf{r}')\Phi(\mathbf{r}') = V_{\mathrm{loc}}(\mathbf{r})\Phi(\mathbf{r})$$

$$
\begin{aligned}
\langle \mathbf{G}_1 \mid V_{\rm loc}(\mathbf{r}) \mid \mathbf{G}_2 \rangle &= \frac{1}{\Omega} \sum_{\mathbf{G}} V_{\rm loc}(\mathbf{G}) \int d\mathbf{r}\; e^{-i\mathbf{G}_1\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}_2\cdot\mathbf{r}} \\
&= \frac{1}{\Omega} \sum_{\mathbf{G}} V_{\rm loc}(\mathbf{G}) \int d\mathbf{r}\; e^{i(\mathbf{G}-\mathbf{G}_1+\mathbf{G}_2)\cdot\mathbf{r}} \\
&= \frac{1}{\Omega} V_{\rm loc}(\mathbf{G}_1 - \mathbf{G}_2) \quad .
\end{aligned}
$$

$$
\begin{aligned}
E_{\rm loc} &= \sum_i f_i \langle \Phi_i \mid V_{\rm loc} \mid \Phi_i \rangle \\
&= \int d\mathbf{r}\; V_{\rm loc}(\mathbf{r})\; n(\mathbf{r}) \\
&= \frac{1}{\Omega} \sum_{\mathbf{G}} V^{\star}_{\rm loc}(\mathbf{G})\; n(\mathbf{G})
\end{aligned}
$$

# Electrostatic Energy

$$
\begin{aligned}
E_{\mathrm{ES}} &= \frac{1}{2}\iint d\mathbf{r}\, d\mathbf{r}'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad + \sum_I \int d\mathbf{r}\, V^I_{\mathrm{core}}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}
\end{aligned}
$$

$$
V^I_{\mathrm{core}}(\mathbf{r}) = \int d\mathbf{r}'\, \frac{n^I_{\mathrm{c}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\mathrm{erf}\left[\frac{|\mathbf{r}-\mathbf{R}_I|}{\mathrm{R}^{\mathrm{c}}_I}\right]
$$

$$
n^I_{\mathrm{c}}(\mathbf{r}) = -\frac{Z_I}{\left(\mathrm{R}^{\mathrm{c}}_I\right)^3}\pi^{-3/2}\exp\left[-\left(\frac{\mathbf{r}-\mathbf{R}_I}{\mathrm{R}^{\mathrm{c}}_I}\right)^2\right]
$$

$$
\begin{aligned}
E_{\rm ES} &= \frac{1}{2}\int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \frac{n_{\rm c}(\mathbf{r})n_{\rm c}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad + \int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \frac{n_{\rm c}(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \frac{1}{2}\int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \frac{n_{\rm c}(\mathbf{r})n_{\rm c}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
\end{aligned}
$$

$$
n_{\rm c}(\mathbf{r}) = \textstyle\sum_I n_{\rm c}^I(\mathbf{r}) \qquad\qquad n_{\rm tot}(\mathbf{r}) = n(\mathbf{r}) + n_{\rm c}(\mathbf{r})
$$

$$
\begin{aligned}
E_{\rm ES} &= \frac{1}{2}\int\!\!\int d\mathbf{r}\, d\mathbf{r}'\, \frac{n_{\rm tot}(\mathbf{r})n_{\rm tot}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\,{\rm erfc}\left[\frac{|\mathbf{R}_I-\mathbf{R}_J|}{\sqrt{{\rm R}_I^{\rm c\,2}+{\rm R}_J^{\rm c\,2}}}\right] - \sum_I \frac{1}{\sqrt{2\pi}}\frac{Z_I^2}{R_I^{\rm c}}
\end{aligned}
$$

$$
\begin{aligned}
n_{\mathrm{tot}}(\mathbf{G}) &= n(\mathbf{G}) + \sum_I n_{\mathrm{c}}^I(\mathbf{G}) S_I(\mathbf{G}) \\
&= n(\mathbf{G}) - \frac{1}{\Omega} \sum_I \frac{Z_I}{\sqrt{4\pi}} \exp\left[-\frac{1}{2} G^2 R_I^{\mathrm{c}\,2}\right] S_I(\mathbf{G})
\end{aligned}
$$

expanded in plane waves with expansion coefficients

$$
S_I(\mathbf{G}) = \exp[-i\mathbf{G} \cdot \mathbf{R}_I]
$$

Structure factor of an atom

the electrostatic energy for a periodic system

$$E_{\mathrm{ES}} = 2\pi\,\Omega \sum_{\mathbf{G}\neq 0} \frac{|n_{\mathrm{tot}}(\mathbf{G})|^2}{G^2} + E_{\mathrm{ovrl}} - E_{\mathrm{self}}$$

$$E_{\mathrm{ovrl}} = \sum_{I,J}{}' \sum_{\mathbf{L}} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|} \mathrm{erfc}\left[\frac{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|}{\sqrt{\mathrm{R}_I^{\mathrm{c}\,2} + \mathrm{R}_J^{\mathrm{c}\,2}}}\right]$$

$$E_{\mathrm{self}} = \sum_I \frac{1}{\sqrt{2\pi}} \frac{Z_I^2}{R_I^{\mathrm{c}}}$$

# Exchange and Correlation Energy

$$E_{\mathrm{xc}} = \int d\mathbf{r}\, \varepsilon_{\mathrm{xc}}(n, \nabla n)\, n(\mathbf{r}) = \Omega \sum_{\mathbf{G}} \varepsilon_{\mathrm{xc}}(\mathbf{G}) n^{\star}(\mathbf{G})$$

Високочестотните компоненти са с млаки амплитуди

$$E_{\mathrm{xc}} = \frac{\Omega}{N_{\mathrm{x}} N_{\mathrm{y}} N_{\mathrm{z}}} \sum_{\mathbf{R}} \varepsilon_{\mathrm{xc}}(n, \nabla n)(\mathbf{R}) n(\mathbf{R}) = \Omega \sum_{\mathbf{G}} \tilde{\varepsilon}_{\mathrm{xc}}(\mathbf{G}) n(\mathbf{G})$$

$\tilde{\varepsilon}_{\mathrm{xc}}(\mathbf{G})$ is the finite Fourier transform of $\varepsilon_{\mathrm{xc}}(\mathbf{R})$.

# Car–Parrinello Equations

$$\mathcal{L} = \mu \sum_i \sum_{\mathbf{G}} |\dot{c}_i(\mathbf{G})|^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E_{\rm KS}\left[\{\mathbf{G}\}, \{\mathbf{R_I}\}\right] + \sum_{ij} \Lambda_{ij} \left( \sum_{\mathbf{G}} c_i^\star(\mathbf{G}) c_j(\mathbf{G}) - \delta_{ij} \right) \quad ,$$

$$\begin{aligned} \mu \ddot{c}_i(\mathbf{G}) &= -\frac{\partial E}{\partial c_i^\star(\mathbf{G})} + \sum_j \Lambda_{ij} c_j(\mathbf{G}) \\ M_I \ddot{\mathbf{R}}_I &= -\frac{\partial E}{\partial \mathbf{R}_I}. \end{aligned}$$

# Velocity Verlet integration algorithm

$$
\begin{aligned}
\tilde{\dot{\mathbf{R}}}_I(t+\delta t) &= \dot{\mathbf{R}}_I(t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t) \\
\mathbf{R}_I(t+\delta t) &= \mathbf{R}_I(t) + \delta t\, \tilde{\mathbf{R}}_I(t+\delta t) \\
\tilde{\dot{\mathbf{c}}}_I(t+\delta t) &= \dot{\mathbf{c}}_I(t) + \frac{\delta t}{2\mu}\mathbf{f}_i(t) \\
\tilde{\mathbf{c}}_i(t+\delta t) &= \mathbf{c}_i(t) + \delta t\, \tilde{\dot{\mathbf{c}}}_i(t+\delta t) \\
\mathbf{c}_i(t+\delta t) &= \tilde{\mathbf{c}}_i(t+\delta t) + \sum_j \mathbf{X}_{ij}\, \mathbf{c}_j(t) \\
\text{calculate} &\quad \mathbf{F}_I(t+\delta t) \\
\text{calculate} &\quad \mathbf{f}_i(t+\delta t) \\
\dot{\mathbf{R}}_I(t+\delta t) &= \tilde{\dot{\mathbf{R}}}_I(t+\delta t) + \frac{\delta t}{2M_I}\mathbf{F}_I(t+\delta t) \\
\dot{\mathbf{c}}'_i(t+\delta t) &= \tilde{\dot{\mathbf{c}}}_i(t+\delta t) + \frac{\delta t}{2\mu}\mathbf{f}_i(t+\delta t) \\
\dot{\mathbf{c}}_i(t+\delta t) &= \dot{\mathbf{c}}'_i(t+\delta t) + \sum_j \mathbf{Y}_{ij}\, \mathbf{c}_j(t+\delta t)
\end{aligned}
$$

$$
\mathbf{X}_{ij} = \frac{\delta t^2}{2\mu}\Lambda^{\mathrm{p}}_{ij}
$$

$$
\mathbf{Y}_{ij} = \frac{\delta t}{2\mu}\Lambda^{\mathrm{v}}_{ij} \ .
$$

# Изисквания за ортогоналност

$$
\begin{aligned}
\mathbf{C}^\dagger(t+\delta t)\mathbf{C}(t+\delta t) - \mathbf{I} &= 0 \\
\left[\tilde{\mathbf{C}} + \mathbf{X}\mathbf{C}\right]^\dagger \left[\tilde{\mathbf{C}} + \mathbf{X}\mathbf{C}\right] - \mathbf{I} &= 0 \\
\tilde{\mathbf{C}}^\dagger\tilde{\mathbf{C}} + \mathbf{X}\tilde{\mathbf{C}}^\dagger\mathbf{C} + \mathbf{C}^\dagger\tilde{\mathbf{C}}\mathbf{X}^\dagger + \mathbf{X}\mathbf{X}^\dagger - \mathbf{I} &= 0 \\
\mathbf{X}\mathbf{X}^\dagger + \mathbf{X}\mathbf{B} + \mathbf{B}^\dagger\mathbf{X}^\dagger &= \mathbf{I} - \mathbf{A}
\end{aligned}
$$

$$
\mathbf{A}_{ij} = \tilde{\mathbf{c}}_i^\dagger(t+\delta t)\tilde{\mathbf{c}}_j(t+\delta t) \text{ and } \mathbf{B}_{ij} = \mathbf{c}_i^\dagger(t)\tilde{\mathbf{c}}_j(t+\delta t)
$$

Итеративна процедура за решаване на последното уравнение

$$
\begin{aligned}
\mathbf{X}^{(n+1)} &= \frac{1}{2}\Big[\mathbf{I} - \mathbf{A} + \mathbf{X}^{(n)}(\mathbf{I} - \mathbf{B}) \\
&\quad + (\mathbf{I} - \mathbf{B})\mathbf{X}^{(n)} - \left(\mathbf{X}^{(n)}\right)^2\Big]
\end{aligned}
$$

$$
\mathbf{X}^{(0)} = \frac{1}{2}(\mathbf{I} - \mathbf{A})
$$

$$\dot{\mathbf{c}}_i^\dagger(t+\delta t)\mathbf{c}_j(t+\delta t) + \mathbf{c}_i^\dagger(t+\delta t)\dot{\mathbf{c}}_j(t+\delta t) = 0$$

$$\mathbf{Y} = -\frac{1}{2}(\mathbf{Q} + \mathbf{Q}^\dagger)$$

$$\mathbf{Q}_{ij} = \mathbf{c}_i^\dagger(t+\delta t)\dot{\mathbf{c}'}_i^\dagger(t+\delta t)$$

# Pseudopotentials

The norm–conserving pseudopotential approach provides an effective and reliable means for performing calculations on complex molecular, liquid and solid state systems using plane wave basis sets. In this approach only the chemically active valence electrons are dealt with explicitely. The inert core electrons are eliminated within the frozen– core approximation, being considered together with the nuclei as rigid non–polarizable ion cores. In turn, all electrostatic and quantum–mechanical interactions of the valence electrons with the cores, as the nuclear Coulomb attraction screened by the core electrons, Pauli repulsion and exchange and correlation between core and valence electrons, are accounted for by angular momentum dependent pseudopotentials.

# Norm–Conserving Pseudopotentials

## Hamann–Schlüter–Chiang Conditions

$$(T + V_{\mathrm{AE}})\,|\Psi_l\rangle = \epsilon_l |\Psi_l\rangle \qquad (T + V_{\mathrm{val}})\,|\Phi_l\rangle = \hat{\epsilon}_l |\Phi_l\rangle$$

1. Real and pseudo valence eigenvalues agree for a chosen prototype atomic configuration. $\epsilon_l = \hat{\epsilon}_l$

2. Real and pseudo atomic wave functions agree beyond a chosen core radius $\mathrm{r}_c$.

$$\Psi_l(r) = \Phi_l(r) \quad \text{for } r \geq r_c$$

3. The integrals from 0 to R of the real and pseudo charge densities agree for $\mathrm{R} \geq \mathrm{r}_c$ for each valence state (norm conservation).

$$\langle \Phi_l | \Phi_l \rangle_R = \langle \Psi_l | \Psi_l \rangle_R \quad \text{for } R \geq r_c$$

where

$$\langle \Phi | \Phi \rangle_R = \int_0^R r^2 |\phi(r)|^2 dr$$

4. The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $\mathrm{r} \geq \mathrm{r}_c$.

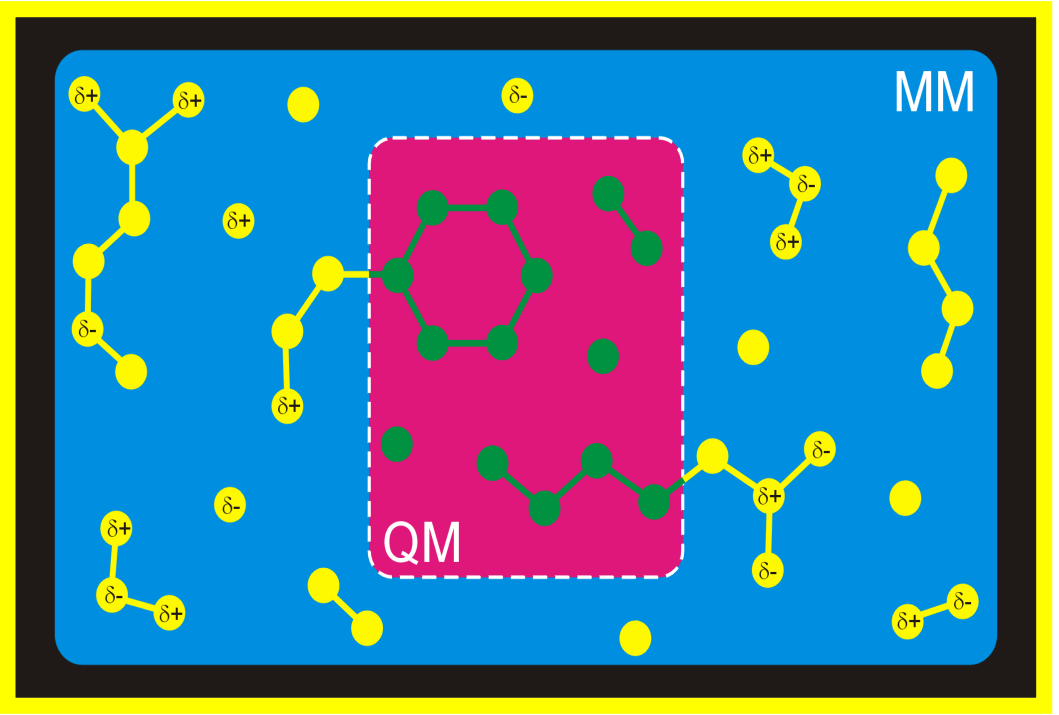
Property 3) and 4) are related through the identity

$$-\frac{1}{2}\left[(r\Phi)^2\frac{d}{d\epsilon}\frac{d}{dr}ln\Phi\right]_R = \int_0^R r^2|\Phi|^2 dr$$

# Квантово-Класически Методи

***Подходящи за описание на:***

- ***Реакции в разтвор***
- ***Ендимни реакции***




Разделяне на посистеми:

- QM – активните центрове
- MM – обкръжаващата ги среда

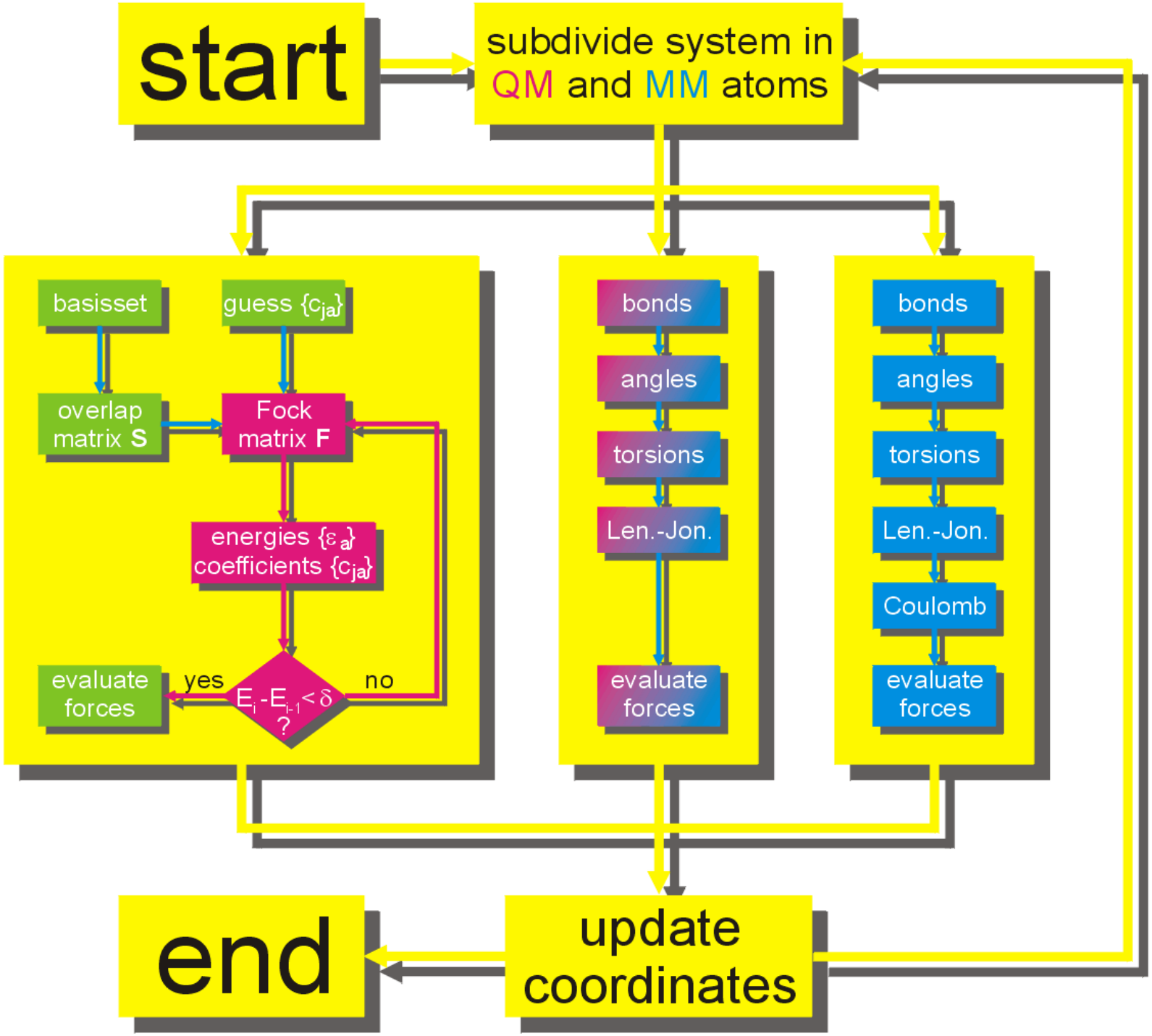
Взаимодеиствията в QM частта – QM хамилтониан

QM/MM – преходна област --- силово поле и QM хамилтониах --- свързваши атоми и замразени орбитали, елекростатични взаимодействия – точкови заряди

Взаимодеиствията в MM частта – MM силово поле

QM/MM хибриден модел:

- Компромис между бързина и точност
- Реалистичност на модела


start
subdivide system in QM and MM atoms
basisset
guess {c_ja}
overlap matrix S
Fock matrix F
energies {ε_a} coefficients {c_ja}
E_i-E_i-1 < δ ?
yes
no
evaluate forces
bonds
angles
torsions
Len.-Jon.
evaluate forces
bonds
angles
torsions
Len.-Jon.
Coulomb
evaluate forces
update coordinates
end
more steps