МЕТОДИ РОЗРАХУНКУ ЕЛЕКТРОННО-ЗБУДЖДЕНИХ СТАНІВ МОЛЕКУЛ

Іванов Володимир Венедиктович

Chemical Materials Department
V. N. Karazin National University,
61077, Kharkov, Ukraine

vivanov@karazin.ua

The Wave functions of excited states

Ground state (equilibrium geometry)

$$\left|\Psi^{0}_{\text{exact}}\right\rangle = 0.9\left|0\right\rangle + 0.1\left|\begin{matrix}a\\i\end{matrix}\right\rangle + 0.2\left|\begin{matrix}ab\\ij\end{matrix}\right\rangle + ...$$

$\left|0\right\rangle$ **- HF ground state**

Excited States

case 1 $$\left|\Psi^{*}_{\text{exact}}\right\rangle = c_0\left|0\right\rangle + c_1\left|\begin{matrix}a\ldots\\i\ldots\end{matrix}\right\rangle + ... \qquad c_1 \sim 0.9 >> c_0$$

case 2 $$\left|\Psi^{*}_{\text{exact}}\right\rangle = c_0\left|0\right\rangle + c_1\left(\left|\begin{matrix}a\\i\end{matrix}\right\rangle \pm \left|\begin{matrix}b\\j\end{matrix}\right\rangle\right) + ... \quad c_1 \sim \frac{1}{\sqrt{2}} >> c_0$$

case 3 $$\left|\Psi^{*}_{\text{exact}}\right\rangle = c_0\left|0\right\rangle + c_1\left(\left|\begin{matrix}ab\\ij\end{matrix}\right\rangle \pm \left|\begin{matrix}cd\\kl\end{matrix}\right\rangle\right) + c_2\left|\begin{matrix}a\\i\end{matrix}\right\rangle + ... \quad c_1 > c_2 > c_0$$

$$\left\langle \Psi^{*}_{\text{exact}} \middle| \Psi^{0}_{\text{exact}} \right\rangle = 0 \qquad \left\langle \Psi^{*}_{i} \middle| \Psi^{*}_{j} \right\rangle = 0$$

Orthogonality condition

Configuration interaction singles, CIS

$$\left|\Psi^{*}_{CIS}\right\rangle = \sum_{i,a} C_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle$$

Brilluene Theorem

$$\left\langle 0 \left| \hat{H} \right| \begin{matrix} a \\ i \end{matrix} \right\rangle = 0$$

$$H_{CIS} = \begin{pmatrix} E_0 & 0 \\ 0 & H_{SS} \end{pmatrix} \qquad H_{SS} = \left\langle \begin{matrix} a \\ i \end{matrix} \left| H \right| \begin{matrix} b \\ j \end{matrix} \right\rangle \qquad \left\langle 0 \left| \hat{H} \right| \Psi^{*}_{CIS} \right\rangle = 0$$

$$H_{CIS} \left|\Psi\right\rangle = E \left|\Psi\right\rangle$$

$$\left|\Psi\right\rangle \rightarrow \left|\Psi\right\rangle = \left|0\right\rangle \qquad E = E_0$$

HF ground state

$$\left|\Psi\right\rangle \rightarrow \left|\Psi\right\rangle = \left|\Psi^{*}_{CIS}\right\rangle = \sum_{i,a} C_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle \qquad E = E_{CIS}$$

Random phase approximation, RPA

Coupled cluster singles, CCS

$$\left|\Psi^{*}_{\mathrm{RPA}}\right\rangle = \left|0\right\rangle + \sum_{i,a} t_i^a \left|\begin{matrix} a \\ i \end{matrix}\right\rangle + \tfrac{1}{2} \sum_{i,j,a,b} t_i^a t_j^b \left|\begin{matrix} ab \\ ij \end{matrix}\right\rangle + \ldots$$

$$\left|\Psi_{\mathrm{RPA}}\right\rangle = \exp(T_1)\left|0\right\rangle$$

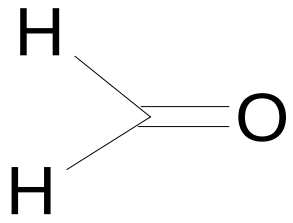
EOM-CCSD

Ground State: $\left|\Psi^0_{\mathrm{CCSD}}\right\rangle = \exp(T_1 + T_2)\left|0\right\rangle$

Excited states $\left|\Psi^*_{\mathrm{EOMCCSD}}\right\rangle = (1 + R_1 + R_2)\exp(T_1 + T_2)\left|0\right\rangle$

$R_1, \quad R_2$ **Single and double excitations against** $\left|\Psi^0_{\mathrm{CCSD}}\right\rangle$

Formaldehyde excited states



	$^3n\pi$ $^3A_2$	$^1n\pi$ $^1A_2$	$^3\pi\pi$ $^3A_1$	$^1\sigma\pi$ $^1B_1$	$^1\pi\pi$ $^1A_1$
CASSCF	3.14	4.36	5.04	9.56	11.31
CIS	3.92	4.77	5.40		10.38
EOMCCSD	-	4.04	-	9.52	10.50
exp.	3.54	4.1	6.0	9.0	10.7

Time Dependent DFT (TD-DFT)

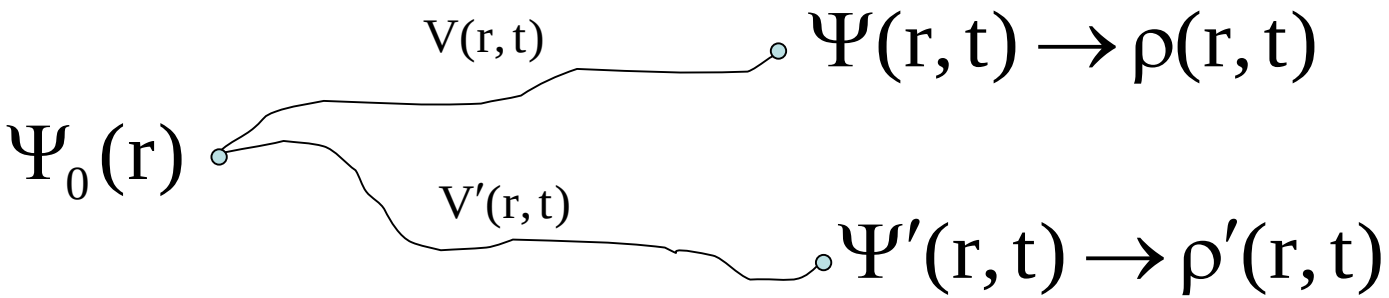
$$V(r,t) = V(r)\cos(\omega t + \varphi)$$

Теорема Runge-Grossa (1984)

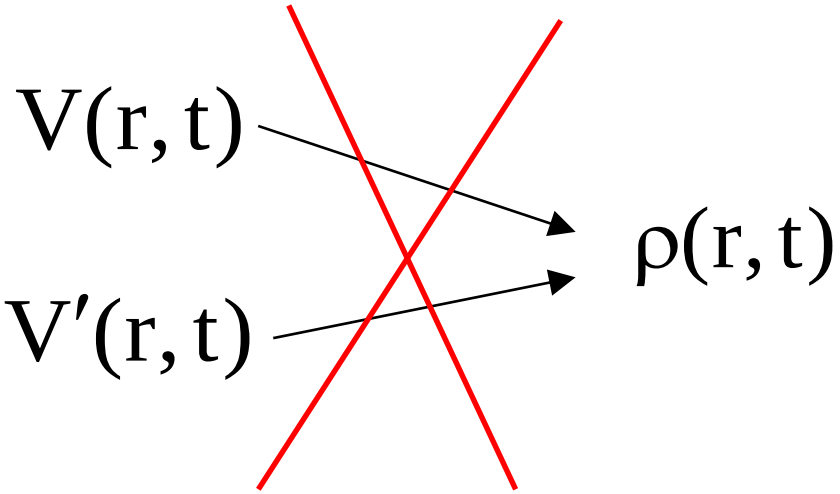
$$V(r,t) \xrightarrow{\Psi_0} \rho(r,t)$$

Single-particle density carries all the information about evolution systems of interacting electrons. It is determined by the potential

Теорема Runge-Grossa



$$i\frac{\partial}{\partial t}\left|\Psi(r,t)\right\rangle = (H + V(r,t))\left|\Psi(r,t)\right\rangle$$



$$V(r,t) \rightarrow \rho(r,t)$$

$$V'(r,t) \rightarrow \rho'(r,t)$$

Теорія лінійного відгуку (Casid equation)

$$\alpha(\omega) = \sum_i \frac{f_i}{\omega_i^2 - \omega^2}$$

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}$$

Spectrum of naphthalene radical cation JCP, 111,1999,p.8904 (eV)

state	UCIS	BLYP	B3LYP	MRCISD	CASPT2	Exp(EA)
$^2B_{2g}$	2.49 (0.65)	2.16 (0.32)	2.15 (0.31)	2.16 (0.32)	1.89 (0.05)	1.84
$^2B_{3g}$	3.53 (0.84)	2.78 (0.09)	2.99 (0.3)	2.94 (0.25)	2.70 (0.01)	2.69
$^2B_{3g}$	3.83 (0.58)	3.53 (0.28)	3.61 (0.36)	3.51 (0.26)	3.24 (-0.01)	3.25
$^2B_{2g}$	4.25 (0.23)	3.75 (-0.27)	3.92 (-0.1)	4.38 (0.36)	3.98 (-0.04)	4.02
$^2B_{2g}$	6.33 (1.78)	4.33 (-0.22)	4.65 (0.1)	5.14 (0.59)	4.44 (-0.11)	4.55
sd	**0.97**	**0.25**	**0.26**	**0.37**	**0.06**	