

A derivation of coupled equations from single-configuration ansatz

Mainz Simulation[†]

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We derive the set of coupled equations from from single-configuration ansatz by Frankel's variational principle.

Key words: TDSCF

The starting point is the non-relativistic quantum mechanics

$$i\hbar \frac{\partial}{\partial t} \Phi(\{r_i\}, \{R_i\}t) = H\Phi(\{r_i\}, \{R_i\}t), \quad (1)$$

in position representation in conjunction with the standard Hamiltonian

$$H = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}(\{r_i\}, \{R_i\}; t) = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + H_e(\{r_i\}, \{R_i\}; t).$$

I. EQUATION OF a

The simplest product ansatz is

$$\Phi(\{r_i\}, \{R_i\}; t) \approx \psi(\{r_i\}, ; t) \chi(\{R_i\}; t) \exp\left[\frac{i}{\hbar} \int_{t_0}^t dt' E_e(t')\right]. \quad (2)$$

Set $\exp[\frac{i}{\hbar} \int_{t_0}^t dt' E_e(t')] = a(t)$, now we derive the equation of a , from left multiplying $\langle \psi \chi |$, $\langle a \psi |$ and $\langle a \chi |$ and integration (Frankel's variational principle [1, 2])

$$\langle \delta \Phi | i \frac{\partial}{\partial t} - H | \Phi \rangle = 0.$$

For convenience, we use Dirac symbols.) In the following expressions, "′" denotes the derivative of time. Inserting (2) into (1) and left multiplying $\langle \psi \chi |$ and integrating (variation with respect to a), we obtain

$$\langle \psi \chi | i a' \psi \chi + i a \psi' \chi + i a \psi \chi' - H a \psi \chi \rangle = 0,$$

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i.e.,

$$ia' = \langle \psi\chi | H | \psi\chi \rangle a - ia \langle \psi | \psi' \rangle - ia \langle \chi | \chi' \rangle.$$

Impose energy conservation $\langle \psi\chi | H | \psi\chi \rangle \equiv \langle H \rangle = E_C$,

$$ia' = E_C a - ia \langle \psi | \psi' \rangle - ia \langle \chi | \chi' \rangle. \quad (3)$$

II. COUPLED EQUATIONS

Multiplying from the left by $\langle a\psi |$ to (1) and integrating (variation with respect to χ), we have

$$\langle a\psi | i \frac{\partial}{\partial t} - H | a\psi\chi \rangle = \langle a\psi | ia' \psi\chi + ia\psi'\chi + ia\psi\chi' - H a\psi\chi \rangle = 0.$$

Because $ia' = E_C a - ia \langle \psi | \psi' \rangle - ia \langle \chi | \chi' \rangle$,

$$i|\chi'\rangle = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 |\chi\rangle + \langle \psi | H_e | \psi \rangle |\chi\rangle + (i\langle \chi | \chi' \rangle - E_C) |\chi\rangle, \quad (4)$$

Similarly, multiplying from the left by $\langle a\chi |$ to (1) and integrating (variation with respect to ψ), we get

$$\langle a\chi | i \frac{\partial}{\partial t} - H | a\psi\chi \rangle = \langle a\chi | ia' \psi\chi + ia\psi'\chi + ia\psi\chi' - H a\psi\chi \rangle = 0.$$

Considering (3), we obtain

$$\langle H \rangle |\psi\rangle - i\langle \psi | \psi' \rangle |\psi\rangle + i|\psi'\rangle - [- \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 |\psi\rangle + \langle \chi | V_{n-e} | \chi \rangle |\psi\rangle] = 0,$$

therefore

$$i|\psi'\rangle = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 |\psi\rangle + \langle \chi | V_{n-e} | \chi \rangle |\psi\rangle + (i\langle \psi | \psi' \rangle - E_C) |\psi\rangle. \quad (5)$$

Since wavefunction (2) is not unique[1, 2], we can choose values of $\langle \psi | \psi' \rangle$ and $\langle \chi | \chi' \rangle$ to uniquely define it. To simplify the coupled equation, we set $i\langle \psi | \psi' \rangle = i\langle \chi | \chi' \rangle = E_C$.

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