A derivation of coupled equations from single-configuration ansatz

Mainz Simulation†

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(Dated: August 18, 2013)

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

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

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

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

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

$$\langle\psi\chi|ia'\psi\chi + ia\psi'\chi + ia\psi\chi' - Ha\psi\chi\rangle = 0,$$

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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

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

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

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

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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