Teori Fungsional Kerapatan

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1 Interaksi Coulomb

Energi interaksi antara dua elektron:

$$E_{\mathrm{ee}} = \frac{e^2}{4\pi\epsilon_0 d_{ee}} \tag{1}$$

Energi interaksi antara dua inti atom dengan nomor atom Z:

$$E_{\mathrm{nn}} = \frac{Z^2 e^2}{4\pi\epsilon_0 d_{\mathrm{nn}}} \tag{2}$$

Energi interaksi antara elektron dan inti atom:

$$E_{\mathrm{en}} = -\frac{Z e^2}{4\pi\epsilon_0 d_{\mathrm{en}}} \tag{3}$$

Persamaan Schroedinger:

$$\left[\frac{\mathbf{p}^2}{2m_e} + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{4}$$

Fungsi gelombang banyak-partikel:

$$\Psi = \Psi\left(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_{N_{\mathrm{at}}}\right) \tag{5}$$

Persamaan Schroedinger banyak-partikel:

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_i \frac{\nabla_I^2}{2M_I} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_i - \mathbf{R}_j|}\right]\Psi = E_{\mathrm{tot}}\Psi \tag{6}$$

Aproksimasi clamped-nuclei:

$$E = E_{\mathrm{tot}} - \frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{7}$$

Persamaan untuk elektron:

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi = E\,\Psi \tag{8}$$

Definisikan:

$$V_\mathrm{n} = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|} \tag{9}$$

sehingga

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_\mathrm{n}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi = E\,\Psi \tag{10}$$

Definisikan Hamiltonian banyak-elektron:

$$\hat{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_\mathrm{n}(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right] \tag{11}$$

Persaman Schroedinger:

$$\hat{H}\,\Psi = E\,\Psi \tag{12}$$

Hamiltonian elektron-tunggal:

$$\hat{H}_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_n(\mathbf{r}) \tag{13}$$

Sehingga Hamiltonian banyak-elektron juga dapat dituliskan menjadi:

$$\hat{H}(\mathbf{r}_1,\ldots,\mathbf{r}_N) = \sum_i \hat{H}_0(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{14}$$

2 Aproksimasi elektron independen

Anggap interaksi Coulomb antara elektron tidak ada.

$$\sum_i \hat{H}_0(\mathbf{r}_i)\,\Psi = E\,\Psi \tag{15}$$

Aproksimasi:

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2)\ldots\phi_N(\mathbf{r}_N) \tag{16}$$

$$\hat{H}_0(\mathbf{r}_i)\phi_i(\mathbf{r}_i) = \varepsilon_i\phi_i \tag{17}$$

$$\left[\sum_i \hat{H}_0(\mathbf{r}_i)\right]\phi_1(\mathbf{r}_1)\ldots\phi_N(\mathbf{r}_N) = E\,\phi_1(\mathbf{r}_1)\ldots\phi_N(\mathbf{r}_N) \tag{18}$$

$$\begin{aligned}\left[\hat{H}_0(\mathbf{r}_1)\phi_1(\mathbf{r})_1\right]\phi_2(\mathbf{r}_2)\ldots\phi_N(\mathbf{r}_N) + \phi_1(\mathbf{r}_1)\left[\hat{H}_0(\mathbf{r}_2)\phi_2(\mathbf{r})_2\right]\ldots\phi_N(\mathbf{r}_N) +\\ \phi_1(\mathbf{r}_1)\ldots\left[\hat{H}_0(\mathbf{r}_N)\phi_N(\mathbf{r})_N\right] = E\,\phi_1(\mathbf{r}_1)\ldots\phi_N(\mathbf{r}_N)\end{aligned}$$

Sehingga:

$$E = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N \tag{19}$$

3 Prinsip ekslusi Pauli

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\right] \tag{20}$$

References