Born-Oppenheimer approximation

$$\hat{\mathcal{H}}\Psi = \frac{-\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2\Psi + \sum_{l=1}^{N}U_{\text{ion}}(\vec{r}_l)\Psi + \sum_{l<l'}\frac{e^2}{|\vec{r}_l - \vec{r}_{l'}|}\Psi = \mathcal{E}\Psi, \tag{L1}$$

“the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble” Dirac, 1929.

Hartree Equations

$$U_{\rm ee}(\vec{r}) = \int d\vec{r}\,' \frac{e^2 n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}, \tag{L2}$$

$$n(\vec{r}) = \sum_j |\psi_j(\vec{r})|^2. \tag{L3}$$

$$\frac{-\hbar^2}{2m}\nabla^2\psi_l + [U_{\rm ion}(\vec{r}) + U_{\rm ee}(\vec{r})]\psi_l = \mathcal{E}_l\psi_l. \tag{L4}$$

Variational Principle

$$F_{\mathcal{H}}\{\Psi\} = \langle\Psi|\hat{\mathcal{H}}|\Psi\rangle, \tag{L5}$$

$$\Psi = \prod_{l=1}^{N} \psi_l(\vec{r}_l), \tag{L6}$$

$$\frac{\delta F_{\mathcal{H}}}{\delta\psi_l^*(\vec{r})} - \frac{\delta}{\delta\psi_l^*(\vec{r})} \sum_j \mathcal{E}_j \int d\vec{r}\,' \psi_j^*(\vec{r}\,')\psi_j(\vec{r}\,') = 0 \tag{L7}$$

Slater determinants

$$\Psi(\vec{r}_1\sigma_1 \ldots \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \sum_s (-1)^s \psi_{s_1}(\vec{r}_1\sigma_1) \ldots \psi_{s_N}(\vec{r}_N\sigma_N) \tag{L8}$$

$$= \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \ldots & \psi_1(\vec{r}_N\sigma_N) \\ . & . & & . \\ . & . & & . \\ . & . & & . \\ . & . & & . \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \ldots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix} . \tag{L9}$$

$$\psi_l(\vec{r}_i\sigma_i) = \phi_l(\vec{r}_i)\chi_l(\sigma_i). \tag{L10}$$

$$\sum_{\sigma_1\ldots\sigma_N}\int d^N\vec{r}\,\frac{1}{N!}\sum_{ss'}(-1)^{s+s'}\left[\prod_j \psi^*_{s_j}(\vec{r}_j\sigma_j)\right]\sum_l \frac{-\hbar^2\nabla_l^2}{2m}\left[\prod_{j'}\psi_{s'_{j'}}(\vec{r}_{j'}\sigma_{j'})\right]. \tag{L11}$$

$$\sum_l\sum_{\sigma_l}\int d\vec{r}_l\,\frac{1}{N!}\sum_s \psi^*_{s_l}(\vec{r}_l\sigma_l)\frac{-\hbar^2\nabla_l^2}{2m}\psi_{s_l}(\vec{r}_l\sigma_l) \tag{L12}$$

$$= \sum_l\sum_{\sigma}\int d\vec{r}\,\frac{1}{N}\sum_{l'}\psi^*_{l'}(\vec{r}\sigma)\frac{-\hbar^2\nabla^2}{2m}\psi_{l'}(\vec{r}\sigma) \tag{L13}$$

$$= \sum_{l=1}^N\int d\vec{r}\phi^*_l(\vec{r})\left[\frac{-\hbar^2\nabla^2}{2m}\right]\phi_l(\vec{r}). \tag{L14}$$

$$\sum_{l=1}^N\int d\vec{r}\phi^*_l(\vec{r})U(\vec{r})\phi_l(\vec{r}). \tag{L15}$$

Hartree-Fock equations

$$\sum_{\sigma_1\ldots\sigma_N}\int d^N\vec{r}\sum_{s,s'}\frac{1}{N!}\sum_{i<j}\frac{e^2(-1)^{s+s'}}{|\vec{r}_i-\vec{r}_j|}\prod_{l,l'}\psi^*_{s_l}(l)\psi_{s'_{l'}}(l') \tag{L16}$$

$$= \sum_{\sigma_1\ldots\sigma_N}\int d^N\vec{r}\sum_{s,s'}\frac{1}{N!}\sum_{i<j}\frac{e^2(-1)^{s+s'}}{|\vec{r}_i-\vec{r}_j|}\left[\begin{array}{ll} & \psi^*_{s_i}(i)\psi^*_{s_j}(j) \\ \times & \psi_{s'_i}(i)\psi_{s'_j}(j) \\ \times & \prod_{l,l'\neq i,j}\psi^*_{s_l}(l)\psi_{s'_{l'}}(l') \end{array}\right] \tag{L17}$$

$$= \sum_{i<j}\sum_{\sigma_i\sigma_j}\int d\vec{r}_i d\vec{r}_j\sum_{s}\frac{1}{N!}\frac{e^2}{|\vec{r}_i-\vec{r}_j|}\left[\begin{array}{l} |\psi_{s_i}(i)|^2|\psi_{s_j}(j)|^2 \\ -\psi^*_{s_i}(i)\psi^*_{s_j}(j)\psi_{s_i}(j)\psi_{s_j}(i) \end{array}\right] \tag{L18}$$

$$= \sum_{\sigma_1\sigma_2}\int\frac{d\vec{r}_1 d\vec{r}_2}{2(N-2)!}\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\sum_{s}\left[\begin{array}{l} |\psi_{s_1}(1)|^2|\psi_{s_2}(2)|^2 \\ -\psi^*_{s_1}(1)\psi^*_{s_2}(2)\psi_{s_1}(2)\psi_{s_2}(1) \end{array}\right] \tag{L19}$$

$$= \sum_{\sigma_1\sigma_2}\int\frac{e^2 d\vec{r}_1 d\vec{r}_2}{|\vec{r}_1-\vec{r}_2|}\sum_{i<j}\left[|\psi_i(1)|^2|\psi_j(2)|^2-\psi^*_i(1)\psi^*_j(2)\psi_i(2)\psi_j(1)\right] \tag{L20}$$

$$= \int \frac{e^2 d\vec{r}_1 d\vec{r}_2}{|\vec{r}_1 - \vec{r}_2|} \sum_{i<j} \left[|\phi_i(\vec{r}_1)|^2 |\phi_j(\vec{r}_2)|^2 - \phi_i^*(\vec{r}_1)\phi_j^*(\vec{r}_2)\phi_i(\vec{r}_2)\phi_j(\vec{r}_1)\delta_{\chi_i \chi_j} \right]. \quad \text{(L21)}$$

Using second quantization

$$\hat{\mathcal{H}} = \sum_{l} \hat{c}_l^\dagger \hat{c}_{l'} \langle l|\hat{K}+\hat{U}_{\rm ion}|l'\rangle + \sum_{ll'l''l'''} \hat{c}_l^\dagger \hat{c}_{l'}^\dagger \hat{c}_{l'''} \hat{c}_{l''} \langle ll'|\hat{U}_{\rm int}|l''l'''\rangle \qquad \text{(L22)}$$

States l label $\psi_l(i) = \phi_l(\vec{r}_i)\chi_l(\sigma_i)$ which include both spatial and spin information.

Second quantization takes this form, no matter what the functions ϕ happen to be. Goal of Hartree-Fock approximation is to find best possible functions.

Find expectation value in ground state

$$|G\rangle = |11111\ldots10000\ldots\rangle \tag{L23}$$

Consider

$$\langle G|\hat{c}_l^\dagger \hat{c}_{l'}|G\rangle \tag{L24}$$

- ☞ Get zero immediately unless l' is one of the states occupied in $|G\rangle$.
- ☞ Then get zero unless l creates again the state that l' has just destroyed.
- ☞ So must have $l \leq N$, $l = l'$, at which point creation and annihilation operators simply disappear.

$$\langle G|\sum_l \hat{c}_l^\dagger \hat{c}_{l'}\langle l|\hat{K}+\hat{U}_{\text{ion}}|l'\rangle|G\rangle = \sum_{l=1}^{N}\langle l|\hat{K}+\hat{U}_{\text{ion}}|l\rangle \tag{L25}$$

Pairing manipulations

Consider

$$\langle G|\hat{c}_l^\dagger \hat{c}_{l'}^\dagger \hat{c}_{l'''} \hat{c}_{l''}|G\rangle \tag{L26}$$

- ☞ Get zero immediately unless l'' and l''' are among the states occupied in $|G\rangle$.
- ☞ Then get zero unless l and l' create again the states that l'' and l''' have just destroyed.
- ☞ If l' recreates state just destroyed by l''' and then l recreates l'' formalism gives overall multiplicative factor of $+1$.
- ☞ However, if l' recreates state destroyed by l'' and then l recreates l''' formalism gives overall multiplicative factor of -1.

$$\langle G| \sum_{ll'l''l'''} \hat{c}_l^\dagger \hat{c}_{l'}^\dagger \hat{c}_{l'''} \hat{c}_{l''} \langle ll'|\hat{U}_{\rm int}|l''l'''\rangle |G\rangle \tag{L27}$$

$$= \sum_{ll'l''l'''} ? \qquad ?\langle ll'|\hat{U}_{\rm int}|l''l'''\rangle \tag{L28}$$

$$= \sum_{ll'} ? \qquad ? \tag{L29}$$

Final result

$$\langle\Psi|\mathcal{H}|\Psi\rangle = \sum_i \sum_{\sigma_1} \int d\vec{r}_1 \psi_i^*(1) \frac{-\hbar^2\nabla^2}{2m} \psi_i(1) + U(\vec{r}_1)|\psi_i(1)|^2$$

$$+ \quad \int d\vec{r}_1 d\vec{r}_2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \sum_{\substack{i<j \\ \sigma_1\sigma_2}} \left[|\psi_i(1)|^2|\psi_j(2)|^2 - \psi_i^*(1)\psi_j^*(2)\psi_i(2)\psi_j(1)\right]. \quad \text{(L30)}$$

Vary with respect to ψ

$\sum_{\sigma_1} \int d\vec{r}_1 \psi_i^*(1)\psi_j(1) = \delta_{ij}$

$$\sum_{i,j} \mathcal{E}_{ij} \sum_{\sigma_1} \int d\vec{r}_1 \psi_i^*(1)\psi_j(1) \tag{L31}$$

$$\sum_j \mathcal{E}_{ij}\psi_j(1) = \left[\begin{array}{l} -\frac{\hbar^2\nabla^2}{2m}\psi_i(1) + U(\vec{r}_1)\psi_i(1) \\ +\psi_i(1) \int d\vec{r}_2 \sum_{\sigma_2, j=1}^{N} \frac{e^2|\psi_j(2)|^2}{|\vec{r}_1 - \vec{r}_2|} \\ -\sum_{j=1}^{N} \psi_j(1) \sum_{\sigma_2} \int d\vec{r}_2 \frac{e^2\psi_j^*(2)\psi_i(2)}{|\vec{r}_1 - \vec{r}_2|} \end{array} \right]. \tag{L32}$$

$$\tilde{\psi}_i = \sum_j W_{ij}\psi_j. \tag{L33}$$

$$\int d\vec{r} \sum_{i\sigma} \tilde{\psi}_i^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} \tilde{\psi}_i(\vec{r}\sigma) \tag{L34}$$

$$= \int d\vec{r} \sum_{i\sigma} \sum_{jj'} W_{ij}^* \psi_j^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} W_{ij'} \psi_{j'}(\vec{r}\sigma) \tag{L35}$$

$$= \int d\vec{r} \sum_{\sigma jj'} \delta_{jj'} \psi_j^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} \psi_j(\vec{r}\sigma) \tag{L36}$$

$$= \int d\vec{r} \sum_{j\sigma} \psi_j^*(\vec{r}\sigma) \frac{-\hbar^2\nabla^2}{2m} \psi_j(\vec{r}\sigma). \tag{L37}$$

$$\sum_{ij} \sum_{ll'} \psi_l^* W_{li}^* \mathcal{E}_{ij} W_{il'} \psi_{l'} \tag{L38}$$

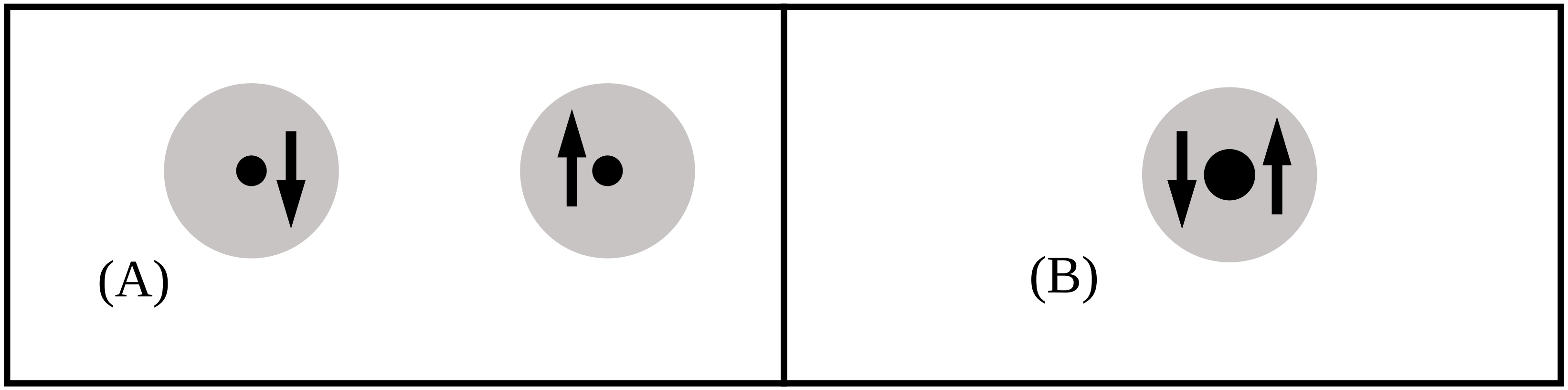
$$= \sum_{ll'} \psi_l \tilde{\mathcal{E}}_{ll'} \psi_{l'}, \tag{L39}$$

where

$$\tilde{\mathcal{E}}_{ll'} = \sum_{ij} W_{li}^{*} \mathcal{E}_{ij} W_{jl'} \quad \text{(L40)}$$

Final equations

$$\mathcal{E}_i\phi_i(\vec{r}) = \left[\begin{array}{l} \dfrac{-\hbar^2\nabla^2}{2m}\phi_i(\vec{r}) + U(\vec{r})\phi_i(\vec{r}) \\ +\phi_i(\vec{r})\displaystyle\int d\vec{r}\,'\sum_{j=1}^{N}\frac{e^2|\phi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} \\ -\displaystyle\sum_{j=1}^{N}\delta_{\chi_i\chi_j}\,\phi_j(\vec{r})\int d\vec{r}\,'\frac{e^2\phi_j^*(\vec{r}\,')\phi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \end{array}\right]. \tag{L41}$$



$$\int d\vec{r} e^{-\lambda_1|\vec{r}-\vec{r}_1|} e^{-\lambda_2|\vec{r}-\vec{r}_2|}, \tag{L42}$$

$$\gamma_l = \sum_{l'} A_{ll'} e^{-a_j\left(\vec{r}-\vec{R}_{l'}\right)^2}, \tag{L43}$$

$$\gamma_1, \gamma_2 \ldots \gamma_K, \tag{L44}$$

$$\phi_l = \sum_{k=1}^{K} B_{lk}\gamma_k, \tag{L45}$$

Practical implementation

Molecule	CH_4	NH_3	H_2O	FH	CO
Bond length (Å): Hartree–Fock	2.048	1.890	1.776	1.696	
Bond length (Å): experiment	2.050	1.912	1.809	1.733	
Ionization potential (eV): Hartree–Fock	0.546	0.428	0.507	0.650	
Ionization potential (eV): experiment	0.529	0.400	0.463	0.581	
Dipole moment (e Å): Hartree–Fock		0.653	0.785	0.764	−0.110
Dipole moment (e Å): experiment		0.579	0.728	0.716	0.044

Jellium

$$\begin{aligned}
&\qquad\quad \textit{Kinetic energy} && \textit{Interaction with ions}\\
\mathcal{E}_l \phi_l(\vec{r}) = &\quad \frac{-\hbar^2\nabla^2}{2m}\phi_l(\vec{r}) && -\phi_l(\vec{r})\frac{N}{\mathcal{V}}\int d\vec{r}_2 \frac{e^2}{|\vec{r}-\vec{r}_2|}\\
&+\phi_l(\vec{r})\int d\vec{r}_2 \sum_{j=1}^{N} \frac{e^2|\phi_j(\vec{r}_2)|^2}{|\vec{r}-\vec{r}_2|} && -\sum_{j=1}^{N}\delta_{\chi_l\chi_j}\phi_j(\vec{r})\int d\vec{r}_2 \frac{e^2\phi_j^*(\vec{r}_2)\phi_l(\vec{r}_2)}{|\vec{r}-\vec{r}_2|}.\\
&\qquad\quad \textit{Coulomb interaction} && \textit{Exchange interaction}
\end{aligned} \tag{L46}$$

$$\phi_l(\vec{r}) = \frac{e^{i\vec{k}_l\cdot\vec{r}}}{\sqrt{\mathcal{V}}}. \tag{L47}$$

Kinetic energy

$$\frac{\hbar^2 k_l^2}{2m}\phi_l(\vec{r}). \tag{L48}$$

$|\phi_j(\vec{r}_2)|^2 = 1/\mathcal{V}$

Exchange

$$e^2 \sum_{j=1}^{N} \frac{e^{i\vec{k}_j \cdot \vec{r}}}{\sqrt{\mathcal{V}}} \int \frac{d\vec{r}_2}{\mathcal{V}} \frac{e^{i(\vec{k}_l - \vec{k}_j)\cdot \vec{r}_2}}{|\vec{r} - \vec{r}_2|} \delta_{\chi_l \chi_j} \tag{L49}$$

$$= e^2 \phi_l \sum_{j=1}^{N} \int \frac{d\vec{r}'}{\mathcal{V}} \frac{e^{i(\vec{k}_l - \vec{k}_j)\cdot \vec{r}'}}{r'} \delta_{\chi_l, \chi_j} \tag{L50}$$

$$= e^2 \phi_l \sum_{j=1}^{N} \frac{1}{\mathcal{V}} \frac{4\pi}{|\vec{k}_l - \vec{k}_j|^2} \delta_{\chi_l, \chi_j} \tag{L51}$$

$$= e^2 \phi_l \int^{k_F} \frac{d\vec{k}}{(2\pi)^3} \frac{4\pi}{k_l^2 + k^2 - 2\vec{k}\cdot\vec{k}_l} \tag{L52}$$

$$= e^2 \phi_l(\vec{r}) \frac{1}{2\pi k_l} \left[\left(k_F^2 - k_l^2\right) \ln \left\{ \frac{k_F + k_l}{k_F - k_l} \right\} + 2k_l k_F \right]. \tag{L53}$$

Energy of jellium, Lindhart dielectric function

$$\mathcal{E}_l = \frac{\hbar^2 k_l^2}{2m} - \frac{2e^2}{\pi} k_F F(k_l/k_F), \tag{L54}$$

$$F(x) = \frac{1}{4x}\left[\left(1-x^2\right)\ln\left\{\frac{1+x}{1-x}\right\} + 2x\right]. \tag{L55}$$

Electron velocity diverges at Fermi surface. Hartree–Fock incorrectly omits effects of screening.

Total energy

$$\mathcal{E} = \sum_l \frac{\hbar^2 k_l^2}{2m} - \frac{e^2}{\pi} k_F F\left(\frac{k_l}{k_F}\right) \quad \text{(L56)}$$

$$= N\left[\frac{3}{5}\mathcal{E}_F - \frac{3}{4}\frac{e^2 k_F}{\pi}\right]. \quad \text{(L57)}$$

$$n(\vec{r}) = \langle\Psi|\sum_{l=1}^{N}\delta(\vec{r}-\vec{R}_l)|\Psi\rangle \tag{L58}$$

$$= N\int d\vec{r}_1\ldots d\vec{r}_N\Psi^*(\vec{r}_1,\vec{r}_2\ldots\vec{r}_N)\delta(\vec{r}-\vec{r}_1)\Psi(\vec{r}_1\ldots\vec{r}_N). \tag{L59}$$

$$\mathcal{E}_1 = \langle\Psi_1|\mathcal{H}_1|\Psi_1\rangle < \langle\Psi_2|\mathcal{H}_1|\Psi_2\rangle \tag{L60}$$

$$\Rightarrow \mathcal{E}_1 < \langle\Psi_2|\mathcal{H}_2|\Psi_2\rangle + \langle\Psi_2|(\hat{\mathcal{H}}_1-\hat{\mathcal{H}}_2)|\Psi_2\rangle \tag{L61}$$

$$\Rightarrow \mathcal{E}_1 < \mathcal{E}_2 + \int d\vec{r}n(\vec{r})\left[U_1(\vec{r})-U_2(\vec{r})\right]. \tag{L62}$$

$$\mathcal{E}_2 < \mathcal{E}_1 + \int d\vec{r}\,n(\vec{r})\left[U_2(\vec{r})-U_1(\vec{r})\right]. \tag{L63}$$

$$\mathcal{E}_1+\mathcal{E}_2 < \mathcal{E}_1+\mathcal{E}_2, \tag{L64}$$

$$\mathcal{E}[n] = T[n]+U[n]+U_{\text{ee}}[n]. \tag{L65}$$

Density functional theory

$$\int d\vec{r}\, n(\vec{r}) = N. \tag{L66}$$

$$\langle \Psi_2 | \mathcal{H}_1 | \Psi_2 \rangle = \mathcal{E}_1[n_2]. \tag{L67}$$

$$\mu = \frac{\delta E[\rho]}{\delta n(\vec{r})}, \tag{L68}$$

$$\mathcal{E}[n] = \int d\vec{r}\, n(\vec{r}) U(\vec{r}) + F_{HK}[n], \tag{L69}$$

$$F_{HK}[n] = T[n] + U_{\mathrm{ee}}[n]. \tag{L70}$$

General derivation

$$F[n] \equiv \min_{\Psi\to n} \langle\Psi|T+U_{ee}|\Psi\rangle. \tag{L71}$$

$$\mathcal{E}_0 = \min_{\Psi} \langle\Psi|T+U+U_{ee}|\Psi\rangle \tag{L72}$$

$$= \min_n [\min_{\Psi\to n} \langle\Psi|T+U+U_{ee}|\Psi\rangle] \tag{L73}$$

$$= \min_n \left[\min_{\Psi\to n} \langle\Psi|T+U_{ee}|\Psi\rangle + \int U(\vec{r})n(\vec{r})d\vec{r}\right] \tag{L74}$$

$$= \min_n \left[F[n] + \int U(\vec{r})n(\vec{r})d\vec{r}\right] \tag{L75}$$

$$\equiv \min_n \mathcal{E}[n]. \tag{L76}$$

$$T = \mathcal{V}\int [d\vec{k}]\,\frac{\hbar^2 k^2}{2m} \tag{L77}$$

$$= \mathcal{V}\frac{\hbar^2 k_F^5}{2m5\pi^2} = \mathcal{V}\frac{\hbar^2}{2m}\frac{3}{5}(3\pi^2)^{2/3}n^{5/3}. \tag{L78}$$

$$\frac{1}{2}\int d\vec{r}_2 d\vec{r}_1 \frac{e^2 n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}. \tag{L79}$$

$$-N\frac{3}{4}\frac{e^2 k_F}{\pi} = -\mathcal{V}\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}. \tag{L80}$$

$$T[n] = \int d\vec{r}\,\frac{\hbar^2}{2m}\frac{3}{5}\left(3\pi^2\right)^{2/3} n^{5/3}(\vec{r}), \tag{L81}$$

$$\mathcal{E}_{xc} = -\int d\vec{r}\,\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}(\vec{r}). \tag{L82}$$

$$\mathcal{E}[n] = \frac{\hbar^2}{2m}\frac{3}{5}\left(3\pi^2\right)^{2/3}\int d\vec{r}\, n^{5/3}(\vec{r}) + \int d\vec{r}\, n(\vec{r})U(\vec{r})$$
$$+ \frac{1}{2}\int d\vec{r}_2 d\vec{r}_1 \frac{e^2 n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} - \int d\vec{r}\,\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} e^2 n^{4/3}(\vec{r}). \quad \text{(L83)}$$

$$\frac{\delta\mathcal{E}}{\delta n(\vec{r})} = \mu \quad \text{(L84)}$$

$$\Rightarrow \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} n^{2/3}(\vec{r}) + U(\vec{r}) + \int d\vec{r}_2 \frac{e^2 n(\vec{r}_2)}{|\vec{r}-\vec{r}_2|} - \left(\frac{3}{\pi}\right)^{1/3} e^2 n^{1/3}(\vec{r}) = \mu. \quad \text{(L85)}$$

Atom of charge Z has energy $-1.5375Z^{7/3}$ Ry

Kohn–Sham equations

$$n(\vec{r}) = \sum_{l=1}^{N} |\psi_l(\vec{r})|^2. \tag{L86}$$

$$T[n] = \sum_l \frac{\hbar^2}{2m} (\nabla\psi_l)^2. \tag{L87}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_l(\vec{r}) + \left[U(\vec{r}) + \int d\vec{r}'\, \frac{e^2 n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \frac{\partial\mathcal{E}_{xc}(n)}{\partial n}\right]\psi_l(\vec{r}) = \mathcal{E}_l\psi_l(\vec{r}). \tag{L88}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi_l(\vec{r}) + \left[U(\vec{r}) + \int d\vec{r}'\, \frac{e^2 n(\vec{r}')}{|\vec{r}-\vec{r}'|} - e^2\left(\frac{3}{\pi}n(\vec{r})\right)^{1/3}\right]\psi_l(\vec{r}) = \mathcal{E}_l(\vec{r}). \tag{L89}$$

Local density approximation

Kohn–Sham equations

Atom	LDA	Hartree–Fock	Experiment
He	−2.83	−2.86	−2.9
Li	−7.33	−7.43	−7.48
Ne	−128.12	−128.55	−128.94
Ar	−525.85	−526.82	−527.60

$$\left[\int d\vec{r}\,\hbar^2|\vec{\nabla}\psi|^2\right]\left[\int d\vec{r}\,r^2|\psi|^2\right] \geq \frac{\hbar^2}{4}; \tag{L90}$$

$$T[n] \geq \frac{\hbar^2}{8m\int d\vec{r}\,r^2 n(\vec{r})}. \tag{L91}$$

$$T[n] \geq \frac{\hbar^2}{2m}\frac{9.116}{(8\pi)^{2/3}}\int d\vec{r}\,n^{5/3}. \tag{L92}$$

$$T[n] = \frac{\hbar^2}{2m}\int d\vec{r}\,|\nabla\psi|^2 \tag{L93}$$

$$T[n] \geq \frac{\hbar^2}{2m}K_s\int d\vec{r}\,n^{5/3}, \tag{L94}$$

$$K_s = 3(\pi/2)^{4/3}, \tag{L95}$$

$$n(\vec{r}) = |\psi(\vec{r})|^2. \tag{L96}$$

$$\frac{\hbar^2}{2m}K_s\int d\vec{r}\,n^{5/3} - \int d\vec{r}\,\frac{e^2 n(\vec{r})}{r}. \tag{L97}$$

$$\lambda(1-\int d\vec{r}\,n) \quad = \quad 0 \tag{L98}$$

is

$$\frac{5}{3}\frac{\hbar^2}{2m}K_s n^{2/3}(\vec{r}) - e^2/r + \lambda \quad = \quad 0. \tag{L99}$$

$$n(\vec{r}) = \begin{cases} \left\{6m[e^2/r - \lambda]/(5K_s\hbar^2)\right\}^{3/2} & \text{for} \quad r < e^2/\lambda \\ 0 & \text{else} \end{cases} . \tag{L100}$$

$$\lambda = \frac{3me^4}{5\hbar^2 K_s}(\frac{\pi^4}{2})^{1/3}; \tag{L101}$$

$$-\frac{9me^4}{10\hbar^2 K_s}(2\pi^2)^{2/3} = -\frac{6}{5}\frac{me^4}{\hbar^2} = -\frac{12}{5}\text{Ry}. \tag{L102}$$