Density Functional Theory and Random Phase Approximation (Fifth-rung correlation functionals)

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Electron Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ext} + \hat{W}$$

Where:

$$\hat{T} = \sum_{j=1}^{N} -\frac{\nabla_j^2}{2}, \;\; \hat{V}_{ext} = \sum_{j=1}^{N} v(\mathbf{r}_j), \;\; \hat{W} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}$$

λ; coupling constant of electron-electron interaction

$$\hat{H}(\lambda) = \hat{T} + \hat{V}^{\lambda} + \lambda \hat{W}$$

Where $0 \leqslant \lambda \leqslant 1$

- $\lambda = 0$: non-interacting particles
- $\lambda = 1$: fully interacting particles

$$H(\lambda) = \begin{cases} \hat{H}_s, & \lambda = 0 \\ \hat{H}, & \lambda = 1 \end{cases}$$

And the single-particle potential ($\hat{V}^{\lambda} = \sum_{j=1}^{N} v^{\lambda}(\mathbf{r}_j)$):

$$V^{\lambda} = \begin{cases} v_s(r) & \lambda = 0 \\ \text{unknown} & 0 < \lambda < 1 \\ v_{ext}(r) & \lambda = 1 \end{cases}$$

Adiabatic Connection Density Functional Theory (ACDFT)

If Φ_0 is wave function of ground state of non-interacting system(H_s):

$$\Phi_0(r_1\sigma_1,...,r_N\sigma_N) = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \varphi_1(r_1\sigma_1) & . & . & . & \varphi_N(r_1\sigma_1) \\ \vdots & & & & \vdots \\ \varphi_1(r_N\sigma_N) & . & . & . & \varphi_N(r_N\sigma_N) \end{pmatrix}$$

And $\Psi_0(\lambda)$ is the ground state of interacting system:

$$\hat{H}(\lambda)|\Psi_0(\lambda)\rangle = E_0(\lambda)|\Psi_0(\lambda)\rangle \quad (1)$$

Then we choose external potential (V^λ) so that the same ground state density is obtained for any interaction strength $\lambda \in [0, 1]$,

ACDFT condition

$$\langle\Psi_0(\lambda)|\hat{n}(\mathbf{r})|\Psi_0(\lambda)\rangle = \langle\Phi_0|\hat{n}(\mathbf{r})|\Phi_0\rangle = n_0(\mathbf{r})$$

A general mistake

E_s:

$$(\hat{T} + \hat{v}_s)\varphi_i = \varepsilon_i\varphi_i$$

$$T_s[n_0] = \sum_i f_i \int d^3r \varphi_i^*(\mathbf{r})\{\varepsilon_i - v_s(\mathbf{r})\}\varphi_i(r) = \sum_i f_i\varepsilon_i - \int v_s(\mathbf{r})n_0(\mathbf{r})d^3r$$

$$E_s = T_s[n_0] + \int v_s(\mathbf{r})n_0(\mathbf{r})d^3r = \sum_i f_i\varepsilon_i$$

E_0:

$$E_0 = T_s[n_0] + E_{\mathrm{ext}}[n_0] + E_H[n_0] + E_{\mathrm{xc}}[n_0]$$

$$E_0 = \sum_i f_i\varepsilon_i - \int v_s(\mathbf{r})n_0(\mathbf{r})d^3r + E_{ext}[n_0] + E_H[n_0] + E_{\mathrm{xc}}[n_0]$$

$$v_s(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_H[n_0](\mathbf{r}) + v_{\mathrm{xc}}[n_0](\mathbf{r})$$

$$E_0 = \sum f_i\varepsilon_i - \int v_{\mathrm{xc}}[n_0](\mathbf{r})n_0(\mathbf{r})d^3r - E_H[n_0] + E_{\mathrm{xc}}[n_0]$$

E_0

$$E_0(\lambda = 1) - E_0(\lambda = 0) = E_0 - E_s = \int_0^1 d\lambda \frac{dE_0(\lambda)}{d\lambda}$$

$$E_0 = E_s + \int_0^1 d\lambda \frac{dE_0(\lambda)}{d\lambda}$$

$$E_0(\lambda) = \left\langle \Psi_0(\lambda) \middle| \hat{H}(\lambda) \middle| \Psi_0(\lambda) \right\rangle, \quad \hat{H} = \hat{T} + \lambda \hat{W} + \hat{V}^\lambda$$

$$\begin{aligned} \frac{d}{d\lambda} E_0(\lambda) &= \left\langle \frac{d\Psi_0(\lambda)}{d\lambda} \middle| \hat{H}(\lambda) \middle| \Psi_0(\lambda) \right\rangle + \left\langle \Psi_0(\lambda) \middle| \hat{H}(\lambda) \middle| \frac{d\Psi_0(\lambda)}{d\lambda} \right\rangle \\ &\quad + \left\langle \Psi_0(\lambda) \middle| \hat{W} + \frac{dV^\lambda}{d\lambda} \middle| \Psi_0(\lambda) \right\rangle \\ &= E_0(\lambda) \left(\left\langle \frac{d\Psi_0(\lambda)}{d\lambda} \middle| \Psi_0(\lambda) \right\rangle + \left\langle \Psi_0(\lambda) \middle| \frac{d\Psi_0(\lambda)}{d\lambda} \right\rangle \right) \\ &\quad + \left\langle \Psi_0(\lambda) \middle| \hat{W} + \frac{dV^\lambda}{d\lambda} \middle| \Psi_0(\lambda) \right\rangle \end{aligned}$$

$$\left\langle \Psi_0(\lambda) \middle| \Psi_0(\lambda) \right\rangle = 0 \Longrightarrow \frac{d}{d\lambda} \left\langle \Psi_0(\lambda) \middle| \Psi_0(\lambda) \right\rangle = 0$$

$$\begin{aligned} \frac{d}{d\lambda} E_0(\lambda) &= \left\langle \Psi_0(\lambda) \middle| \hat{W} + \frac{dV^\lambda}{d\lambda} \middle| \Psi_0(\lambda) \right\rangle \\ &= \left\langle \Psi_0(\lambda) \middle| \hat{W} \middle| \Psi_0(\lambda) \right\rangle + \frac{d}{d\lambda} \left\langle \Psi_0(\lambda) \middle| V^\lambda \middle| \Psi_0(\lambda) \right\rangle \end{aligned}$$

$$
\begin{aligned}
&\int_0^1 d\lambda \, \frac{d}{d\lambda} \left\langle \Psi_0(\lambda) \middle| V^\lambda \middle| \Psi_0(\lambda) \right\rangle \\
&= \left\langle \Psi_0 \middle| V_{\rm ext} \middle| \Psi_0 \right\rangle - \left\langle \Phi_0 \middle| V_s \middle| \Phi_0 \right\rangle \\
&= \int d^3r \; n_0(\mathbf{r})[v_{\rm ext}(\mathbf{r}) - v_s(\mathbf{r})]
\end{aligned}
$$

$$
E_0 = E_s + \int d^3r \; n_0(\mathbf{r})[v_{\rm ext}(\mathbf{r}) - v_s(\mathbf{r})] + \int_0^1 d\lambda \left\langle \Psi_0(\lambda) \middle| \hat{W} \middle| \Psi_0(\lambda) \right\rangle
$$

$$
\begin{aligned}
E_0 &= E_s - \int d^3r\ n_0(\mathbf{r})v_s(\mathbf{r}) + \int d^3r\ n_0(\mathbf{r})v_{\rm ext} + \int_0^1 d\lambda\langle\Psi_0(\lambda)|\hat{W}|\Psi_0(\lambda)\rangle \\
&= T_s[n_0] + \int d^3r\ n_0(\mathbf{r})v_{\rm ext} + \int_0^1 d\lambda\langle\Psi_0(\lambda)|\hat{W}|\Psi_0(\lambda)\rangle
\end{aligned}
$$

On the other hand:

$$
E_0 = T_s[n_0] + \int d^3r\ n_0(\mathbf{r})v_{\rm ext} + E_H[n_0] + E_{\rm xc}[n_0]
$$

$$
E_{\rm xc}[n_0] = \int_0^1 d\lambda\langle\Psi_0(\lambda)|\hat{W}|\Psi_0(\lambda)\rangle - \frac{1}{2}\int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}
$$

Density Operator

$$\hat{n}(\mathbf{r}) = \sum_{l=1}^{N} \delta(\mathbf{r} - \mathbf{r}_l)$$
$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$$

$$\begin{aligned}
n(\mathbf{r}) \quad &= \int \Psi_0^*(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \Psi_0(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) d^3r_2 d^3r_3 ... d^3r_N \\
&+ \int \Psi_0^*(\mathbf{r}_1, \mathbf{r}, \mathbf{r}_3, ..., \mathbf{r}_N) \Psi_0(\mathbf{r}_1, \mathbf{r}, \mathbf{r}_3, ..., \mathbf{r}_N) d^3r_1 d^3r_3 ... d^3r_N \\
&+ \int \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}, ..., \mathbf{r}_N) \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}, ..., \mathbf{r}_N) d^3r_1 d^3r_2 ... d^3r_N \\
&... \\
&= \int \delta(\mathbf{r} - \mathbf{r}_1) \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) d^3r_1 d^3r_2 d^3r_3 ... d^3r_N \\
&+ \int \delta(\mathbf{r} - \mathbf{r}_2) \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) d^3r_1 d^3r_2 d^3r_3 ... d^3r_N \\
&+ \int \delta(\mathbf{r} - \mathbf{r}_3) \Psi_0^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N) d^3r_1 d^3r_2 d^3r_3 ... d^3r_N \\
&...
\end{aligned}$$

$$\langle\Psi_0(\lambda)|\hat{W}|\Psi_0(\lambda)\rangle = \langle\Psi_0(\lambda)|\frac{1}{2}\sum_{\substack{j,k\\ j\neq k}}\frac{1}{|\mathbf{r}_j-\mathbf{r}_k|}|\Psi_0(\lambda)\rangle$$
$$= \frac{1}{2}\sum_{\substack{j,k\\ j\neq k}}\int \Psi^*_{0_\lambda}(\mathbf{r}_1,...,\mathbf{r}_j,...,\mathbf{r}_k,...,\mathbf{r}_N)\frac{1}{|\mathbf{r}_j-\mathbf{r}_k|}\Psi_{0_\lambda}(\mathbf{r}_1,...,\mathbf{r}_j,...,\mathbf{r}_k,...,\mathbf{r}_N)d^3r_1...d^3r_N$$
$$= \frac{1}{2}\int\int\frac{1}{|\mathbf{r}-\mathbf{r}'|}d^3r d^3r' \sum_{\substack{j,k\\ j\neq k}}\langle\Psi_0(\lambda)|\delta(\mathbf{r}-\mathbf{r}_j)\delta(\mathbf{r}'-\mathbf{r}_k)|\Psi_0(\lambda)\rangle$$

$$\sum_{\substack{j,k\\ j\neq k}}\langle\Psi_0(\lambda)|\delta(\mathbf{r}-\mathbf{r}_j)\delta(\mathbf{r}'-\mathbf{r}_k)|\Psi_0(\lambda)\rangle$$
$$= \sum_{j,k}\langle\Psi_0(\lambda)|\delta(\mathbf{r}-\mathbf{r}_j)\delta(\mathbf{r}'-\mathbf{r}_k)|\Psi_0(\lambda)\rangle - \delta(\mathbf{r}-\mathbf{r}')\sum_{j}\langle\Psi_0(\lambda)|\delta(\mathbf{r}-\mathbf{r}_j)|\Psi_0(\lambda)\rangle$$
$$= \langle\Psi_0(\lambda)|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle - \delta(\mathbf{r}-\mathbf{r}')\langle\Psi_0(\lambda)|\hat{n}(\mathbf{r})|\Psi_0(\lambda)\rangle$$

$$
\begin{aligned}
\delta\hat{n}(\mathbf{r}) &= \hat{n}(\mathbf{r}) - n(\mathbf{r}) \\
\hat{n}(\mathbf{r}) &= n(\mathbf{r}) + \delta\hat{n}(\mathbf{r})
\end{aligned}
$$

$$\langle\Psi_0(\lambda)|\hat{n}(\mathbf{r})|\Psi_0(\lambda)\rangle = n(\mathbf{r}) \Longrightarrow \langle\Psi_0|\delta\hat{n}(\mathbf{r})|\Psi_0\rangle$$

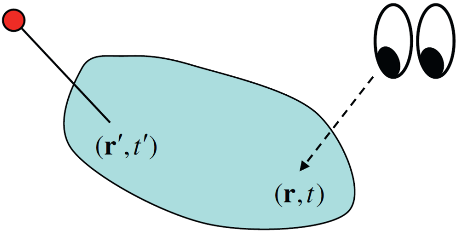
$$\langle\Psi_0(\lambda)|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle = \langle\Psi_0(\lambda)|\delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle + n(\mathbf{r})n(\mathbf{r}')$$

$$E_{\mathrm{xc}}[n_0] = \frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}[\langle\Psi_0(\lambda)|\delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle - \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})]$$

”The idea now is that the **correlations** represented by the **fluctuation** term which are caused by interactions between the electrons, and the description of this physics is rather subtle: **IF** a fluctuation occurs, it will cause some interaction energy beyond the Hartree description.”

Idea: Replacing IF with WHEN

"It is easier conceptually, and helpful in the construction of approximation schemes, to relate this process to the interaction between the non-random density changes caused when an small externally-controlled field is applied. Thus we are led to introduce time-dependent density response theory, and we have converted a tricky IF scenario into a conceptually simpler WHEN scenario. The mathematical tool that justifies this shift in philosophy is the fluctuation- dissipation theorem, described in sufficient generality (i.e. for two unequal operators) in the book by Landau and Lifshitz (1969). For completeness we now give a simple direct derivation of the frequency integrated, zero-temperature form of the theorem needed here."



Response Function

$$\hat{H}(t) = H_0 + H_1(t), \quad \hat{H}_1(t) = F(t)\hat{\beta}$$
$$\alpha_0 = \langle\Psi_0|\hat{\alpha}|\Psi_0\rangle$$
$$\alpha(t) = \langle\Psi(t)|\hat{\alpha}|\Psi(t)\rangle$$
$$\alpha(t) - \alpha_0 = \alpha_1(t) + \alpha_2(t) + \ldots$$

$$\alpha_1(t) = \int_{-\infty}^{\infty} dt' \chi_{\alpha\beta}(t-t')F(t')$$

$$\chi_{\alpha\beta}(t-t') = -i\Theta(t-t')\langle\Psi_0|[\hat{\alpha}(t-t'), \hat{\beta}]|\Psi_0\rangle$$

$$\chi_{\alpha\beta}(\omega) = -i\int_{-\infty}^{\infty} \Theta(\tau)\langle\Psi_0|[\hat{\alpha}(\tau), \hat{\beta}]|\Psi_0\rangle e^{i\omega\tau}$$

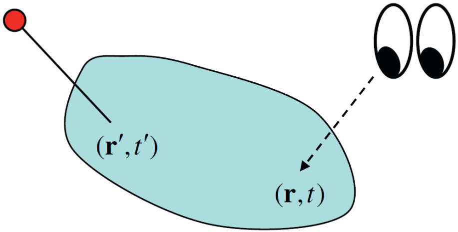
Lehmann representation of the linear response function

$$\sum_{n=0}^{\infty} |\Psi_n\rangle\langle\Psi_n| = 1, \quad \Theta(\tau) = \lim_{\eta\to 0^+} \frac{1}{2\pi} \int_{-\infty}^{-\infty} d\omega' \frac{e^{-i\omega'}}{\omega' + i\eta}$$

$$\chi_{\alpha\beta}(\omega) = \lim_{\eta\to 0^+} \sum_{n=1}^{\infty} \left\{ \frac{\langle\Psi_0|\hat{\alpha}|\Psi_n\rangle\langle\Psi_n|\hat{\beta}|\Psi_0\rangle}{\omega - \Omega_n + i\eta} - \frac{\langle\Psi_0|\hat{\beta}|\Psi_n\rangle\langle\Psi_n|\hat{\alpha}|\Psi_0\rangle}{\omega + \Omega_n + i\eta} \right\}$$

Where Ψ_n is *n*th excited state of interacting system with energy E_n and $\Omega_n = E_n - E_0$

Density density response



$$\hat{H}_1(t) = \int d^3r' v_1(\mathbf{r}', t)\hat{n}(\mathbf{r}')$$

$$n_1(\mathbf{r}, t) = \int_{-\infty}^{\infty} dt' \int d^3r' \chi_{nn}(\mathbf{r}, \mathbf{r}', t - t')v_1(\mathbf{r}', t')$$

$$\chi_{nn}(\mathbf{r}, \mathbf{r}', t - t') = -i\theta(t - t')\langle\Psi_0|[\hat{n}(\mathbf{r}, t - t'), \hat{n}(\mathbf{r}')]|\Psi_0\rangle$$

$$\chi_{nn}(\omega) = \lim_{\eta\to 0^+} \sum_{n=1}^{\infty} \left\{ \frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_n\rangle\langle\Psi_n|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\omega - \Omega_n + i\eta} - \frac{\langle\Psi_0|\hat{n}(\mathbf{r}')|\Psi_n\rangle\langle\Psi_n|\hat{n}(\mathbf{r})|\Psi_0\rangle}{\omega + \Omega_n + i\eta} \right\}$$

From the fluctuation-dissipation theorem:

$$\langle\Psi_0(\lambda)|\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle = n(\mathbf{r})n(\mathbf{r}') - \frac{1}{\pi}\int_0^\infty d\omega \Im\chi^\lambda(\mathbf{r},\mathbf{r}',\omega)$$

Or

$$\langle\Psi_0(\lambda)|\delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle = -\frac{1}{\pi}\int_0^\infty d\omega \Im\chi^\lambda(\mathbf{r},\mathbf{r}',\omega)$$

$$E_{xc}[n_0] = \frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}[\langle\Psi_0(\lambda)|\delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}')|\Psi_0(\lambda)\rangle - \delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})]$$

$$E_{xc}[n_0] = -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + \frac{1}{\pi}\int_0^\infty d\omega \Im\chi^\lambda(\mathbf{r},\mathbf{r}',\omega)\right\}$$

"The first term looks a bit problematic owing to the presence of the delta function; however, we can get rid of it by splitting $E_{xc}[n]$ into exchange and correlation parts, $E_x[n]$ and $E_c[n]$."

KS Density-Density response function and E_{x}

$$\chi_s(\mathbf{r},t,\mathbf{r}',t') = \frac{\delta n[v_s](\mathbf{r},t)}{\delta v_s(\mathbf{r}',t')}\Big|_{v_s[n_0](\mathbf{r})}$$

Lehmann representation of the KS linear response function:

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_{j,k=1}^{\infty}(f_k - f_j)\frac{\varphi_j(\mathbf{r})\varphi_k^*(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{\omega - \omega_{jk} + i\eta}$$

If $\chi_s(\mathbf{r},\mathbf{r}',\omega) \mapsto \chi(\mathbf{r},\mathbf{r}',\omega)$:

$$E_{\mathrm{x}}[n_0] = -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + \frac{1}{\pi}\int_0^{\infty} d\omega \Im\chi_s(\mathbf{r},\mathbf{r}',\omega)\right\}$$

Exact representation of E_{c}

$$E_{\mathrm{c}}[n_0] = E_{\mathrm{xc}}[n_0] - E_{\mathrm{x}}[n_0]$$

$$E_{\mathrm{c}}[n_0] = -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty \frac{d\omega}{2\pi}\left\{\Im\chi_s(\mathbf{r},\mathbf{r}',\omega) - \Im\chi^\lambda(\mathbf{r},\mathbf{r}',\omega)\right\}$$

$$E_{\mathrm{c}}[n_0] = -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\int_0^\infty \frac{du}{2\pi}\left\{\chi_s(\mathbf{r},\mathbf{r}',iu) - \chi^\lambda(\mathbf{r},\mathbf{r}',iu)\right\}$$

Dyson equation

Exchange-Correlation Kernel:

$$f_{\mathrm{xc}}^{\lambda}(\mathbf{r},t,\mathbf{r}',t') = \frac{\delta v_{\mathrm{xc}}^{\lambda}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\Big|_{n_0(\mathbf{r})}$$

Dyson equation for $\chi^{\lambda}(\mathbf{r},\mathbf{r}',\omega)$:

$$\chi^{\lambda}(\mathbf{r},\mathbf{r}',\omega) = \chi_s(\mathbf{r},\mathbf{r}',\omega) + \int d^3x \int d^3x' \chi_s(\mathbf{r},\mathbf{x},\omega)\Big\{\frac{\lambda}{|\mathbf{x}-\mathbf{x}'|} + f_{\mathrm{xc}}^{\lambda}(\mathbf{x},\mathbf{x}',\omega)\Big\}\chi^{\lambda}(\mathbf{x}',\mathbf{r}',\omega)$$

"Any approximation to $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',\omega)$ will immediately give an approximation to E_{c}"

Random Phase Approximation (RPA)

$f_{xc}^{\lambda} = 0 \Longrightarrow \text{RPA}$

$$\chi_{\text{RPA}}^{\lambda}(\mathbf{r},\mathbf{r}',\omega) = \chi_s(\mathbf{r},\mathbf{r}',\omega) + \int d^3x \int d^3x' \chi_s(\mathbf{r},\mathbf{x},\omega) \frac{\lambda}{|\mathbf{x}-\mathbf{x}'|} \chi_{\text{RPA}}^{\lambda}(\mathbf{x}',\mathbf{r}',\omega)$$

The λ-integration can be carried out analytically, and one finds:

$$E_{\text{c}}^{\text{RPA}} = \int_0^{\infty} \frac{du}{2\pi} \int d^3r \int d^3r' \Big\{ \frac{\chi_s(\mathbf{r},\mathbf{r}',iu)}{|\mathbf{r}-\mathbf{r}'|} + \ln[\delta(\mathbf{r}-\mathbf{r}') - \int d^3r'' \frac{\chi_s(\mathbf{r}'',\mathbf{r}',iu)}{|\mathbf{r}-\mathbf{r}''|}] \Big\}$$

RPA problem

Table 14.1 Molecular atomization energies (in kcal/mol), obtained with the RPA, TDHF, and ACFD functionals [eqns (14.16) and (14.17)]. The xc kernel was calculated in the adiabatic approximation based on various ground-state xc functionals. All RPA and ACFD energies were evaluated with PBE Kohn–Sham orbitals (Furche and Van Voorhis, 2005).

	RPA	TDHF	f_{xc}^{ALDA}	f_{xc}^{PBE}	f_{xc}^{BP86}	f_{xc}^{B3LYP}	f_{xc}^{PBE0}	Experiment
CH_4	405	416	426	426	419	408	422	419
CO	244	249	287	287	286	258	264	259
F_2	31	22	74	63	76	42	43	39
H_2	109	108	110	110	107	110	111	109
H_2O	224	226	249	245	241	230	235	232
NH_3	290	289	296	293	286	285	297	297

RPA problem

”Depending on the particular implementation and choice of basis functions, one can achieve a scaling of order N^4 to N^6 , where N is the number of valence electrons.”

References

- Time-Dependent Density-Functional Theory, by Carsten Ullrich (2012)