Summary so far

1) Hohenberg-Kohn Theorem

- gs densities and external potentials in 1-1 correspondence (i.e. gs density uniquely determines ext. potential)

$$n(\vec{r}) \overset{1-1}{\longleftrightarrow} v(\vec{r}) \quad \leadsto |\Psi\rangle = |\Psi[v]\rangle = |\Psi[v[n]]\rangle$$

- HK variational principle:
in order to find gs density $n_0(r)$ corresponding to ext. potential $v_0(r)$, minimize

$$E_{v_0}[n] = F^{HK}[n] + \int d^3r\, n(\vec{r})\, v_0(\vec{r})$$

F^{HK}: universal fctl, indep. of $v_0(\vec{r})$

$$F^{HK}[n] = \min_{\Psi \to n(\vec{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

2) KS theorem

the gs density $n_0(\vec{r})$ of an interacting system (in pot. $v_0(\vec{r})$) can be reproduced (under assumption of "non-interacting v-representability") as density of an auxiliary, non-int. system, the KS system

$$\left(-\frac{\nabla^2}{2} + v_s(\vec{r})\right) \varphi_i(\vec{r}\sigma) = \varepsilon_i\, \varphi_i(\vec{r}\sigma)$$

$$n_{0,s}(\vec{r}) = n_0(\vec{r}) = \sum_{i=1}^{N} |\varphi_i(\vec{r}\sigma)|^2$$

with $v_s(\vec{r}) = v_0(\vec{r}) + \int d^3r' \frac{n_0(\vec{r}')}{|\vec{r}-\vec{r}'|} + \overbrace{\left.\frac{\delta E_{xc}[n]}{\delta n(\vec{r})}\right|_{n=n_0(r)}}^{v_{xc}[n](\vec{r})}$

and xc energy

$$E_{xc}[n] = F^{HK}[n] - \frac{1}{2}\int dr \int dr' \frac{n(r)n(r')}{|\vec{r}-\vec{r}'|} - T_s[n]$$

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V-Representability and N-Representability

Def: A function $n(\vec{r})$ is called pure-state v representable if it is the density of a (possibly degenerate) ground state of a Hamiltonian $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{U}$ with suitably chosen external potential $v(\vec{r})$.

Question: are all "reasonably well behaved" (non-negative) functions $n(\vec{r})$ integrating to N pure-state v-representable ?

Answer: No (Levy, PRA 26, 1200 (1982),
Lieb, e.g., Int. J. Quant. Chem. 24, 243 (1983))

consider system with q indep. degenerate gs $|\Psi_1\rangle, \ldots |\Psi_q\rangle$

construct statistical density matrix

$$\hat{D} = \sum_{i=1}^{q} d_i \, |\Psi_i\rangle\langle\Psi_i| \qquad d_i = d_i^* \geq 0, \; \sum_{i=1}^{q} d_i = 1$$

calculate ensemble density

$$n_D(\vec{r}) = \mathrm{tr}\{\hat{D}\,\hat{n}(\vec{r})\} = \sum_{i=1}^{q} d_i \; n_i(\vec{r})$$

with $\quad n_i(\vec{r}) = \langle\Psi_i|\hat{n}(\vec{r})|\Psi_i\rangle$

in general, function $n_D(\vec{r})$ is not pure-state v-representable.

But $n_D(\vec{r})$ is still associated with an external potential and functions of this form are called "ensemble v-representable".

Not all well-behaved non-negative functions are ensemble v-representable (Englisch/Englisch, Physica **121 A**, 253 (1983))

However, on a (finite or infinite) grid which is strictly positive, normalized and consistent with Pauli principle ($n(\vec{r})$ at any lattice site $\vec{r}$ is smaller than the number of spin states) is ensemble v-representable.

<u>N-Representability</u>:

consider HK (actually Levy-Lieb) functional

$$F^{HK}[n] = F^{LL}[n] = \min_{\Psi \to n(\vec{r})} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$

i.e. $F^{LL}[n]$ is defined for all densities which can be represented as density of some antisymmetric N-particle function (not necessarily the gs of any Hamiltonian). Such functions are called {pure-state} N-representable.

extension of $F^{LL}[n]$ based on density matrix:

$$F^{L}[n] = \min_{\hat{D} \to n(\vec{r})} tr\{\hat{D}(\hat{T} + \hat{V}_{ee})\}$$

$$\hat{D} = \sum_{i=1}^{\infty} d_i \, |\Psi_i\rangle\langle\Psi_i|$$

$$d_i = d_i^* \geq 0 \qquad \sum_{i=1}^{\infty} d_i = 1$$

$$n(\vec{r}) = tr\{\hat{D}\,\hat{n}(\vec{r})\} = \sum_{i=1}^{\infty} d_i \langle \Psi_i | \hat{n}(\vec{r}) | \Psi_i \rangle$$

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All non-negative functions $n(\vec{r})$ (normalized to N) are (pure-state) N-representable

Proof by construction in 1D (Harriman, PR A **24**, 680 (1981))

given $n(x)$ (≥ 0) with $\int_{-\infty}^{\infty} dx\, n(x) = N$

define function $f(x)$ through $\frac{df(x)}{dx} = \frac{2\pi}{N} n(x)$

$$\rightsquigarrow f(x) = \frac{2\pi}{N} \int_{-\infty}^{x} dy\, n(y)$$

define set of sp orbitals

$$\varphi_k(x) = \sqrt{\frac{n(x)}{N}}\, e^{i(k f(x) + \phi(x))} \qquad \text{with } k \in \mathbb{Z}$$

and $\phi(x)$ arbitrary real-valued fct of x

φ_k are orthonormal:

$$\int_{-\infty}^{\infty} dx\, \varphi_{k'}^*(x)\varphi_k(x) = \int_{-\infty}^{\infty} dx \frac{n(x)}{N} e^{i(k-k')f(x)} = \int_{-\infty}^{+\infty} dx \frac{1}{2\pi}\frac{df}{dx} e^{i(k-k')f(x)}$$

$$= \frac{1}{2\pi}\int_0^{2\pi} df\, e^{i(k-k')f} = \delta_{kk'}$$

and form complete set

$$\sum_{k\in\mathbb{Z}} \varphi_k(x)\varphi_k^*(y) = e^{i[\phi(x)-\phi(y)]}\frac{1}{N}\sqrt{n(x)n(y)}\sum_{k=-\infty}^{\infty} e^{ik(f(x)-f(y))}$$

$$= e^{i[\phi(x)-\phi(y)]}\frac{2\pi}{N}\sqrt{n(x)n(y)}\,\delta(f(x)-f(y))$$

$$= \frac{2\pi}{N} n(x) \frac{\delta(x-y)}{\left|\frac{df(x)}{dx}\right|} = \delta(x-y)$$

↳ Slater determinants

$$\chi_{k_1 \ldots k_N} = \frac{1}{\sqrt{N!}} \det\{\varphi_{k_1}, \ldots, \varphi_{k_N}\} \qquad k_1, \ldots k_N \in \mathbb{Z} \quad k_i \neq k_j \text{ for } i \neq j$$

form complete orthonormal set of N-particle functions, all with density

$$\langle \chi_{k_1 \ldots k_N} | \hat{n}(x) | \chi_{k_1 \ldots k_N} \rangle$$

$$= \sum_{i=1}^{N} |\varphi_{k_i}(x)|^2 = \sum_{i=1}^{N} \frac{n(x)}{N} = n(x) \qquad \#$$

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