Density-potential functionals and Wigner functions

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UCLA 1981–1985

Papers with Schwinger on
the refinements of the
Thomas–Fermi model of the atom:
Phys. Rev. A **26**, 2322 (1982);
29, 2331 & 2339 & 2353 (1984);
32, 26 & 36 & 47 (1985).

Later work includes
Phys. Rev. A **45**, 127 (1992);
63, 033606 (2001)^a;
83, 052517 (2011)^b
with ^{a}K. Góral, K. Rzążewski,
and ^{b}B. Fang.

Julian Schwinger
1918–1994

Effective potential energy; mixed functionals — 1

Begin with Hohenberg–Kohn (1964),

$$E_{\mathrm{gs}} = \min_{n} E[n] \quad \text{with} \quad E[n] = E_{\mathrm{kin}}[n] + \int (d\mathbf{r}) V_{\mathrm{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{\mathrm{int}}[n]$$

$$\text{and the constraint} \quad N = \int (d\mathbf{r}) n(\mathbf{r}) \,.$$

Then incorporate the constraint with the aid of a Lagrange multiplier,

$$E_{\mathrm{gs}} = \operatorname*{extr}_{n,\zeta} E[n,\zeta] \quad \text{with} \quad E[n,\zeta] = E[n] - \zeta N + \zeta \int (d\mathbf{r}) n(\mathbf{r}) \,,$$

and introduce the *effective potential energy* $V(\mathbf{r})$ in accordance with

$$\delta E_{\mathrm{kin}}[n] = -\int (d\mathbf{r}) \left[V(\mathbf{r}) + \zeta \right] \delta n(\mathbf{r}) \quad \text{or} \quad V(\mathbf{r}) = -\frac{\delta}{\delta n(\mathbf{r})} E_{\mathrm{kin}}[n] - \zeta \,.$$

Then, $E_1 = E_{\mathrm{kin}}[n] + \int (d\mathbf{r}) n(\mathbf{r}) \left[V(\mathbf{r}) + \zeta \right]$ is a functional of $V(\mathbf{r}) + \zeta$, because

$$\delta E_1 = \int (d\mathbf{r}) n(\mathbf{r}) \left[\delta V(\mathbf{r}) + \delta\zeta \right] .$$

Effective potential energy; mixed functionals — 2

We now have

$$E_{\mathrm{gs}} = \operatorname*{extr}_{V,n,\zeta} E[V,n,\zeta]$$

with the *density-potential functional*

$$E[V,n,\zeta] = E_1[V+\zeta] - \int (d\mathbf{r}) \big[V(\mathbf{r}) - V_{\mathrm{ext}}(\mathbf{r})\big] n(\mathbf{r}) + E_{\mathrm{int}}[n] - \zeta N\,.$$

The extremum condition implies

$$\begin{aligned}
&\text{(a)} \quad \delta V(\mathbf{r}): \quad n(\mathbf{r}) = \frac{\delta}{\delta V(\mathbf{r})} E_1[V+\zeta]\,,\\
&\text{(b)} \quad \delta n(\mathbf{r}): \quad V(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + \frac{\delta}{\delta n(\mathbf{r})} E_{\mathrm{int}}[n]\,,\\
&\text{(c)} \quad \delta\zeta: \quad N = \frac{\partial}{\partial\zeta} E_1[V+\zeta]\,.
\end{aligned}$$

We get $E[V,n,\zeta] \to E[n,\zeta]$ upon enforcing (a); we get $E[V,n,\zeta] \to E[n]$ ("density functional") upon enforcing (a) and (c); we get $E[V,n,\zeta] \to E[V,\zeta]$ ("potential functional") upon enforcing (b).

Effective potential energy; mixed functionals — 3

Example: Atomic Thomas–Fermi functionals, $V_{\text{ext}} = -\dfrac{Z}{r}$ (in atomic units).

$$E^{\text{TF}}[V,n,\zeta] = \underbrace{\int(d\mathbf{r})\left(-\frac{1}{15\pi^2}\right)\left(-2\left[V(\mathbf{r})+\zeta\right]\right)^{5/2}}_{=E_1^{\text{TF}}[V+\zeta]} - \int(d\mathbf{r})\left(V(\mathbf{r})+\frac{Z}{r}\right)n(\mathbf{r})$$

$$+\underbrace{\frac{1}{2}\int(d\mathbf{r})(d\mathbf{r}')\frac{n(\mathbf{r})n(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|}}_{=E_{\text{int}}^{\text{TF}}[n]} - \zeta N$$

implies

$$\text{(a)}\quad \delta V(\mathbf{r}):\quad n(\mathbf{r}) = \frac{1}{3\pi^2}\left(-2\left[V(\mathbf{r})+\zeta\right]\right)^{3/2},$$

$$\text{(b)}\quad \delta n(\mathbf{r}):\quad V(\mathbf{r}) = -\frac{Z}{r} + \int(d\mathbf{r}')\frac{n(\mathbf{r}')}{\left|\mathbf{r}-\mathbf{r}'\right|},$$

$$\text{(c)}\quad \delta\zeta:\quad N = \int(d\mathbf{r})\frac{1}{3\pi^2}\left(-2\left[V(\mathbf{r})+\zeta\right]\right)^{3/2}.$$

Enforcing (a) gives $E^{\text{TF}}[n,\zeta]$ with $E_{\text{kin}}^{\text{TF}}[n] = \int(d\mathbf{r})\frac{1}{10\pi^2}\left[3\pi^2 n(\mathbf{r})\right]^{5/3}$, while enforcing (b) gives

Effective potential energy; mixed functionals — 4

$$E^{\mathrm{TF}}[V,\zeta] = E_1^{\mathrm{TF}}[V+\zeta] - \frac{1}{8\pi}\int (d\mathbf{r})\left[\boldsymbol{\nabla}\left(V(\mathbf{r}) + \frac{Z}{r}\right)\right]^2 - \zeta N\,.$$

Note that

$$E_{\mathrm{gs}}^{\mathrm{TF}} = \min_{n} E^{\mathrm{TF}}[n] \quad \text{with constraint} \quad N = \int (d\mathbf{r})\, n(\mathbf{r})\,,$$

whereas

$$E_{\mathrm{gs}}^{\mathrm{TF}} = \max_{V,\zeta} E^{\mathrm{TF}}[V,\zeta]\,.$$

For $N = Z$, this gives simple upper and lower bounds on Baker's constant B in $E_{\mathrm{gs}}^{\mathrm{TF}} = -\frac{3B}{7a}Z^{7/3}$ with $a = \frac{1}{2}\left(\frac{3\pi}{4}\right)^{2/3} = 0.8853$.

Significance of $E_1[V+\zeta]$:

$$E_1[V+\zeta] = E_{\mathrm{kin}}[n] + \int (d\mathbf{r})n(\mathbf{r})\big[V(\mathbf{r}) + \zeta\big] = \langle \mathrm{gs}|\sum_{j=1}^{N}\big[H(\hat{\mathbf{p}}_j,\hat{\mathbf{r}}_j) + \zeta\big]|\mathrm{gs}\rangle$$

with the single-particle Hamiltonian $H(\mathbf{p},\mathbf{r}) = \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{r})$.

Effective potential energy; mixed functionals — 5

Significance of $E_1[V+\zeta]$:

$$E_1[V+\zeta] = \langle\mathrm{gs}|\sum_{j=1}^{N}\Big[\underbrace{\frac{1}{2m}\hat{\mathbf{p}}_j^2 + V(\hat{\mathbf{r}}_j)}_{=H(\hat{\mathbf{p}}_j,\,\hat{\mathbf{r}}_j)}+\zeta\Big]|\mathrm{gs}\rangle = \mathrm{tr}\{f(H+\zeta)\}$$

with a single-particle trace of a function of $H+\zeta$ that one needs to determine (or guess).

The noninteracting-particles approximation $f(H+\zeta) \simeq (H+\zeta)\eta(-H-\zeta)$ has a very good track record ("put one fermion each into the eigenstates of H with eigenvalues $H' < -\zeta$").

We can use Wigner functions to evaluate the trace, for example

$$\mathrm{tr}\{f(H+\zeta)\} = 2\int\frac{(\mathrm{d}\mathbf{r})\,(\mathrm{d}\mathbf{p})}{(2\pi\hbar)^3}\big[f(H+\zeta)\big]_{\mathrm{W}}(\mathbf{r},\mathbf{p})$$

for spin-$\frac{1}{2}$ fermions with no spin preference. Here, $\big[f(H+\zeta)\big]_{\mathrm{W}}(\mathbf{r},\mathbf{p}) \simeq f\big(H(\mathbf{p},\mathbf{r})+\zeta\big)$ is the extreme semiclassical approximation that reproduces the TF version of $E_1[V+\zeta]$.

Effective potential energy; mixed functionals — 6

History

1– E. H. Lieb
Density Functionals for Coulomb Systems
Int. J. Qu. Chem. **24**, 243–277 (1983)

2– BGE
Energy functionals and the Thomas–Fermi model in momentum space
Phys. Rev. A **45**, 127–134 (1992)
precursor: pages 104–110 in LNP **300** (1988); $E[V, n, \zeta]$ is used much there

3– W. Yang, P. W. Ayers, Q. Wu
Potential Functionals: Dual to Density Functionals and Solution to the v-Representability Problem
Phys. Rev. Lett. **92**, 146404 (2004) [4 pages]

4– A. Cangi, E. K. U. Gross, K. Burke
Potential functionals versus density functionals
eprint arXiv:1307.4235 (2013) [16 pages]

Confession: I don't really understand many of the details in papers 1,3,4 and don't know how their approaches are related to mine.

Approximate Wigner functions — 1

Question: Given operator A and its Wigner function A_{W}, how do we express the Wigner function of a function of A in terms of A_{W}? That is: $\left[g(A)\right]_{\mathrm{W}} = ?$

Extreme semiclassical approximation (TF): $\left[g(A)\right]_{\mathrm{W}} \simeq g(A_{\mathrm{W}})$.

Leading quantum correction:

$$\left[g(A)\right]_{\mathrm{W}} \simeq g(A_{\mathrm{W}}) - \frac{\hbar^2}{16}\{A_{\mathrm{W}}\Lambda^2 A_{\mathrm{W}}\}g''(A_{\mathrm{W}}) + \frac{\hbar^2}{24}\{A_{\mathrm{W}}\Lambda A_{\mathrm{W}}\Lambda A_{\mathrm{W}}\}g'''(A_{\mathrm{W}})$$

where Λ is the two-sided differential operator of the Poisson bracket,

$$\{F\Lambda G\} = \frac{\partial F}{\partial \mathbf{r}} \cdot \frac{\partial G}{\partial \mathbf{p}} - \frac{\partial F}{\partial \mathbf{p}} \cdot \frac{\partial G}{\partial \mathbf{r}}\,.$$

Alternatively one can use

$$\left[g(A)\right]_{\mathrm{W}} \simeq \int \mathrm{d}x\, \mathrm{Ai}(x)\left[f(A_{\mathrm{W},x}) - \frac{\hbar^2}{16}\{A_{\mathrm{W}}\Lambda^2 A_{\mathrm{W}}\}f''(A_{\mathrm{W},x})\right]$$

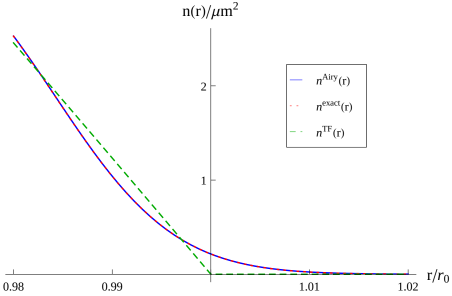
with $A_{\mathrm{W},x} = A_{\mathrm{W}} + \frac{x}{2}\left[\hbar^2\{A_{\mathrm{W}}\Lambda A_{\mathrm{W}}\Lambda A_{\mathrm{W}}\}\right]^{1/3}$.

Approximate Wigner functions — 2

These order-$(\hbar\Lambda)^2$ approximations are pretty good and quite sufficient for many applications. If the transition $E[V, n, \zeta] \to E[n]$ is made, they reproduce the known von Weizsäcker corrections to the kinetic energy in 3D and 1D and give a corresponding term ($\neq 0$) in 2D.

For the perturbative evaluation of the contribution to the ground-state energy and other purposes, it is better, however, to stick to the potential functional.

Example: Density $n(\mathbf{r}) = 2\int \frac{(\mathrm{d}\mathbf{p})}{(2\pi\hbar)^D}\left[\eta(-H-\zeta)\right]_{\mathrm{W}}(\mathbf{r},\mathbf{p}) \simeq \cdots$



(by Martin Trappe)

Approximate Wigner functions — 3

The interaction energy $E_{\mathrm{int}} = \int (\mathrm{d}\mathbf{r})(\mathrm{d}\mathbf{r}')V_{\mathrm{int}}(\mathbf{r}-\mathbf{r}')n^{(2)}(\mathbf{r},\mathbf{r}';\mathbf{r},\mathbf{r}')$ needs the diagonal part of the two-particle density matrix, which can be approximated (reasonably well) in terms of the one-particle density matrix (Dirac 1930),

$$n^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_1',\mathbf{r}_2') \simeq n^{(1)}(\mathbf{r}_1;\mathbf{r}_1')n^{(1)}(\mathbf{r}_2;\mathbf{r}_2') - \frac{1}{2}n^{(1)}(\mathbf{r}_1;\mathbf{r}_2')n^{(1)}(\mathbf{r}_2;\mathbf{r}_1')$$

and we get the one-particle density matrix $n^{(1)}(\mathbf{r};\mathbf{r}')$ from the corresponding Wigner function $\nu(\mathbf{r},\mathbf{p})$,

$$n^{(1)}(\mathbf{r};\mathbf{r}') = \int \frac{(\mathrm{d}\mathbf{p})}{(2\pi\hbar)^3}\,\nu\big(\tfrac{1}{2}(\mathbf{r}+\mathbf{r}'),\mathbf{p}\big)\mathrm{e}^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar}\,,$$

where we can use the TF approximation

$$\nu(\mathbf{r},\mathbf{p}) \simeq 2\eta\big(P(\mathbf{r})^2 - \mathbf{p}^2\big)\Big|_{3\pi^2\hbar^3 n = P^3} = 2\eta\big([3\pi^2\hbar^3 n(\mathbf{r})]^{2/3} - \mathbf{p}^2\big)\,.$$

This is good enough for many purposes, and one can improve on it if one wishes.

THANK YOU