Local Exchange Potentials: A Mathematical Viewpoint

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Hartree-Fock exchange operator

- Density matrix $\gamma_\Phi(\mathbf{r},\mathbf{r}') = \sum_{i=1}^N \phi_i(\mathbf{r})\phi_i(\mathbf{r}')$, electronic density $\rho_\Phi(\mathbf{r}) = \gamma_\Phi(\mathbf{r},\mathbf{r})$;
- **Hatree-Fock minimization problem**

$$I^{\rm HF} = \inf\left\{E^{\rm HF}(\Phi),\ \Phi\in\mathcal{X}_N\right\} \qquad \text{with } \mathcal{X}_N = \left\{\Phi=(\phi_i)_{1\le i\le N}\in (H^1(\mathbb{R}^3))^N \ \middle|\ \int_{\mathbb{R}^3}\phi_i\phi_j = \delta_{ij}\right\},$$

$$E^{\rm HF}(\Phi) = \frac12\sum_{i=1}^N\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}V_{\rm nuc}\rho_\Phi + \frac12\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{\rho_\Phi(\mathbf{r})\rho_\Phi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' - \frac12\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{|\gamma_\Phi(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'.$$

- Hartree-Fock equations $\begin{cases}\left(-\frac12\Delta + V_{\rm nuc} + \rho_\Phi\star\frac{1}{|\mathbf{r}|} + K_\Phi\right)\phi_i = \epsilon_i\phi_i,\\ \epsilon_1\le\epsilon_2\le\cdots\le\epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \mathcal{F}_\Phi;\end{cases}$
- **Hartree-Fock exchange operator** $(K_\Phi\phi)(\mathbf{r}) = -\int_{\mathbb{R}^3}\frac{\gamma_\Phi(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\phi(\mathbf{r}')\,d\mathbf{r}'$.

Approximate exchange potentials as results of minimization problems

Consider $\Phi=(\phi_i)_{1\le i\le N}\in\mathcal{X}_N$. How to approximate K_Φ?

Slater exchange potential [10]

- **Definition.** Introduced by Slater as some average potential $v_{x,S}^\Phi(\mathbf{r}) = -\frac{1}{\rho_\Phi(\mathbf{r})}\int_{\mathbb{R}^3}\frac{|\gamma_\Phi(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$.
- **Variational definition.** If $\rho_\Phi>0$ almost everywhere, the Slater potential $v_{x,S}^\Phi$ is the unique minimizer of the variational problem

$$\boxed{\inf\left\{\frac12\|(v-K_\Phi)\gamma_\Phi\|_{\mathfrak{S}_2}^2,\ v\in L^3(\mathbb{R}^3)+\mathrm{L}^\infty(\mathbb{R}^3)\right\}}$$

- **Asymptotic behavior.** Since $-\int_{\mathbb{R}^3}\frac{\rho_\Phi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' \le v_{x,S}^\Phi(\mathbf{r}) \le 0$, the potential $v_{x,S}^\Phi\to0$ when $|\mathbf{r}|\to+\infty$. If the orbitals ϕ_i are radial or there exists $1\le p<3/2<q\le2$ such that $|\mathbf{r}|\rho_\Phi\in L^p(\mathbb{R}^3)\cap L^q(\mathbb{R}^3)$, the asymptotic behavior of the Slater potential is $v_{x,S}^\Phi(\mathbf{r}) = -\frac{1}{|\mathbf{r}|} + \mathrm{o}\left(\frac{1}{|\mathbf{r}|}\right)$;
- SCF solutions to $\begin{cases}\left(-\frac12\Delta + V_{\rm nuc} + \rho_\Phi\star\frac{1}{|\mathbf{r}|} + v_{x,S}^\Phi\right)\phi_i = \epsilon_i\phi_i, \qquad \int_{\mathbb{R}^3}\phi_i\phi_j=\delta_{ij},\\ \epsilon_1\le\cdots\le\epsilon_N \text{ are the lowest } N \text{ eigenvalues of } \left(-\frac12\Delta + V_{\rm nuc} + \rho_\Phi\star\frac{1}{|\mathbf{r}|} + v_{x,S}^\Phi\right)\end{cases}$, for radial orbitals for a single nucleus of charge $Z\ge N$ (fixed point strategy inspired by [6]).

Effective Local Potential (ELP) [11, 4]

- **Definition.** Definition through the minimization of $v\mapsto S_\Phi(v) = \sum_{i=1}^N\sum_{a=N+1}^{+\infty}|\langle\phi_i\,|\,(v-K_\Phi)\,|\,\phi_a\rangle|^2$ (see [11]), which can be reformulated in a more intrinsic way as

$$\boxed{\inf\left\{\frac12\|[v-K_\Phi,\gamma_\Phi]\|_{\mathfrak{S}_2}^2,\ v\in L^3(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)\right\}}$$

  where $[A,B]=AB-BA$ denotes the commutator of the operators A and B.
- **Analytical expression.** Any solution $v_{x,\rm ELP}^\Phi$ to the ELP minization problem satisfies

$$\rho_\Phi(\mathbf{r})v_{x,\rm ELP}^\Phi(\mathbf{r}) = -\int_{\mathbb{R}^3}\frac{|\gamma_\Phi(\mathbf{r},\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' + \sum_{i,j=1}^N\left(\langle\phi_i|v_{x,\rm ELP}^\Phi|\phi_j\rangle - \langle\phi_i|K_\Phi|\phi_j\rangle\right)\phi_i(\mathbf{r})\,\phi_j(\mathbf{r})$$

and the symmetric matrix $M^\Phi = \left[\langle\phi_i|v_{x,\rm ELP}^\Phi|\phi_j\rangle\right]$ is solution to the linear system

$$(I-A^\Phi)M^\Phi = G^\Phi, \qquad A_{kl,ij}^\Phi = \int_{\mathbb{R}^3}\frac{\phi_i\,\phi_j\,\phi_k\,\phi_l}{\rho_\Phi}, \qquad G_{kl}^\Phi = \int_{\mathbb{R}^3}v_{x,S}^\Phi\phi_k\phi_l - \sum_{i,j=1}^N A_{kl,ij}^\Phi\langle\phi_i|K_\Phi|\phi_j\rangle.$$

Besides, if the orbitals ϕ_i are continuous and if the open set $\mathbb{R}^3\setminus\rho_\Phi^{-1}(0)$ is connected, then $v_{x,\rm ELP}^\Phi$ is uniquely defined, up to an additive constant, on the set where $\rho_\Phi>0$, and can be given arbitrary values on $\rho_\Phi^{-1}(0)$.

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Optimized Effective Potential

Original formulation of the OEP problem

- **Formal definition of the OEP potential [9, 12].** Consider the Slater determinant based on $\Phi^W = (\phi_1^W,\dots,\phi_N^W)$, which are the first N eigenfunctions of H_W, and minimize the Hartree-Fock energy $E^{\rm HF}(\Phi^W)$:

$$\Phi^{\rm OEP} \leftrightarrow \operatorname{argmin}\left\{E^{\rm HF}(\Phi^W),\ (\phi_1^W,\dots,\phi_N^W) \text{ are the first } N \text{ eigenfunctions of } -\frac12\Delta + W\right\};$$

- Exchange part of a potential W defined as $v_x^W = W - V_{\rm nuc} - \rho_{\gamma_W}\star\frac{1}{|\mathbf{r}|}$, where $\gamma_W=\gamma_{\Phi^W}$;
- **Well-posed reformulation** of the OEP problem [1]: eliminate W from the formulation of the problem

Rigorous formulation of the integral OEP equation

Assumption 1 *Potential $W\in L^2(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$, Hamiltonian operator H_W bounded from below, defined on the domain $D(H_W)=H^2(\mathbb{R}^3)$, self-adjoint on $L^2(\mathbb{R}^3)$ with at least N eigenvalues (including multiplicities) below its essential spectrum, gap*

$$\eta = \epsilon_{N+1}^W - \epsilon_N^W > 0$$

between ϵ_N^W (the N-th eigenvalue of H_W) and ϵ_{N+1}^W (the $(N+1)$-th eigenvalue of H_W, or the bottom of the essential spectrum if H_W has only N eigenvalues below its essential spectrum).

Theorem 2 (Integral OEP equation) *Let W be a local potential such that Assumption 1 holds true. Then, for $w\in\mathcal{B}_{\eta/2} = \left\{w\in L^1(\mathbb{R}^3)\cap L^\infty(\mathbb{R}^3),\ \|w\|_{L^1\cap L^\infty}<\eta/2\right\}$*

$$\gamma_{W+w} = \operatorname{arginf}\left\{\mathrm{Tr}\,(H_{W+w}\gamma),\ \gamma\in\mathcal{P}_N\right\} = \chi_{(-\infty,\epsilon_F]}(H_{W+w}),$$

with $\epsilon_F = (\epsilon_N^W+\epsilon_{N+1}^W)/2$. There exists a unique function $\varrho^W\in L^2(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$ such that

$$\boxed{E^{\rm HF}(\gamma_{W+w}) = E^{\rm HF}(\gamma_W) + \int_{\mathbb{R}^3}\varrho^W w + \mathrm{O}\left(\|w\|_{L^1\cap L^\infty}^2\right).}$$

In particular, the function $w\mapsto E^{\rm HF}(\gamma_{W+w})$ is Fréchet differentiable on $\mathcal{B}_{\eta/2}$. Denoting by $R^0(z) = (z-H_W)^{-1}$ the resolvent of H_W and by $\mathcal{C}$ a regular closed contour enclosing the lowest N eigenvalues of H_W, the function ϱ^W is the unique fonction of $L^2(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)$ such that for all $w\in L^1(\mathbb{R}^3)\cap L^\infty(\mathbb{R}^3)$,

$$\boxed{\mathrm{Tr}\left(\frac{1}{2\pi\mathrm{i}}\oint_{\mathcal{C}}(K_{\gamma_W}-v_x^W)R^0(z)wR^0(z)\,dz\right) = \int_{\mathbb{R}^3}\varrho^W w.}$$

A necessary condition for a local potential W satisfying Assumption 1 to be an OEP is $\varrho^W=0$ a.e.

Approximations of the integral OEP equation

- **Discrete spectrum.** When the spectrum of H_W is purely discrete: $R^0(z) = \sum_{n=1}^{+\infty}\frac{|\phi_n^W\rangle\langle\phi_n^W|}{z-\epsilon_n^W}$.
  Usual (formal) OEP optimality condition recovered $\sum_{i=1}^N\sum_{a=N+1}^{+\infty}\frac{\langle\phi_i^W\,|\,K_{\Phi^W}-v_x^W\,|\,\phi_a^W\rangle}{\epsilon_i^W-\epsilon_a^W}\phi_i^W(\mathbf{r})\,\phi_a^W(\mathbf{r}) = 0$.
  Nothing known on existence/uniqueness of solutions.
- **KLI potential [5].** Approximation $\sum_{i=1}^N\sum_{j\in\mathbb{N}^*,\,j\ne i}\langle\phi_i^W\,|\,K_{\Phi^W}-v_{x,\rm KLI}^{\Phi^W}\,|\,\phi_j^W\rangle\,\phi_i^W(\mathbf{r})\,\phi_j^W(\mathbf{r}) = 0$.
  The KLI potential is the unique solution, up to an additive constant, to the minimization problem $\inf\left\{\frac12\left(\|\gamma_\Phi(v-K_\Phi)\|_{\mathfrak{S}_2}^2 - \sum_{i=1}^N|\langle\phi_i|(v-K_\Phi)|\phi_i\rangle|^2\right),\ v\in L^3(\mathbb{R}^3)+L^\infty(\mathbb{R}^3)\right\}$.
- **CEDA potential [2].** Approximation $R^0(z) = (z-H_W)^{-1}\simeq R_{\rm CEDA}^0(z) = (z-H_W^{\rm CEDA})^{-1}$ with

$$H_W^{\rm CEDA} = \underline{\epsilon}\gamma_{\Phi^W} + \overline{\epsilon}\,(1-\gamma_{\Phi^W}),$$

  where $\underline{\epsilon}$ and $\overline{\epsilon}$ lay respectively inside and outside $\mathcal{C}$. Coincides with local Hartree-Fock (LHF) exchange potential [8] and with the self-consistent effective local potential [4].

Some important mathematical definitions

- **Hilbert-Schmidt operator.** $T\in\mathcal{L}(L^2(\mathbb{R}^3))$ is Hilbert-Schmidt if and only if there exists a function of $L^2(\mathbb{R}^3\times\mathbb{R}^3)$ such that $(Tu)(\mathbf{r}) = \int_{\mathbb{R}^3}T(\mathbf{r},\mathbf{r}')\,u(\mathbf{r}')\,d\mathbf{r}'$. In this case, $\|T\|_{\mathfrak{S}_2} = \left(\int_{\mathbb{R}^3\times\mathbb{R}^3}|T(\mathbf{r},\mathbf{r}')|^2\,d\mathbf{r}\,d\mathbf{r}'\right)^{1/2}$.
- **Self-adjoint operator.** The adjoint of T is the unique linear operator on $L^2(\mathbb{R}^3)$ defined by

$$D(T^*) = \left\{u\in L^2(\mathbb{R}^3)\ \middle|\ \exists v_u\in L^2(\mathbb{R}^3) \text{ such that } \langle v_u,w\rangle = \langle u,Tw\rangle\ \forall w\in D(T)\right\}$$
$$T^*u = v_u \qquad (v_u \text{ is uniquely defined since } D(T) \text{ is dense in } L^2(\mathbb{R}^3)).$$

  The operator T is called self-adjoint if $T^*=T$ (*i.e.* if $D(T^*)=D(T)$ and $\forall u\in D(T)=D(T^*)$, $T^*u=Tu$).
- **Resolvent set and spectrum.** If $z-T$ is an invertible operator from $D(T)$ to $L^2(\mathbb{R}^3)$, it can be proved that $R(z)=(z-T)^{-1}$ defines a continuous linear operator on $L^2(\mathbb{R}^3)$ (with range $D(T)$). The set $\rho(T) = \left\{z\in\mathbb{C}\ |\ z-T \text{ is an invertible operator from } D(T) \text{ to } L^2(\mathbb{R}^3)\right\}$ is called the resolvent set of T. The spectrum of T is the set $\sigma(T)=\mathbb{C}\setminus\rho(T)$.
  The spectrum $\sigma(T)$ of a self-adjoint operator can be partitioned as $\sigma(T)=\sigma_{\rm d}(T)\cup\sigma_{\rm ess}(T)$, where $\sigma_{\rm d}(T)$ is the set of all the isolated eigenvalues of T of finite multiplicity, and where $\sigma_{\rm ess}(T)=\sigma(T)\setminus\sigma_{\rm d}(T)$.
  Example: $\sigma_{\rm ess}\left(-\frac12\Delta - \sum_{k=1}^K\frac{Z_k}{|\mathbf{r}-\mathbf{R}_k|}\right) = [0,+\infty)$, $\sigma_{\rm d}\left(-\frac12\Delta - \sum_{k=1}^K\frac{Z_k}{|\mathbf{r}-\mathbf{R}_k|}\right) = \{\epsilon_0,\dots,\epsilon_n,\dots\}$, $\epsilon_n\to0$.