A mean-field model of the relativistic atom

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Relativistic quantum chemistry

When $Z \geq 26$ (Iron) the energies of the core electrons in an atom enter in the relativistic regime. As a consequence, models based on the nonrelativistic kinetic operator $-\Delta$ may lead to wrong predictions. For example, nonrelativistic models predict that:

-Gold is white.

-Lead is as hard as Diamond.

-Mercury is solid at room temperature.

Relativistic models give the correct predictions, but their use is much more delicate. They are based on the Dirac operator, which is not bounded below.

The Dirac operator

The free Dirac operator ('28):

$$\boxed{D^0 = -ic\sum_{k=1}^{3}\alpha_k\partial_k + \beta mc^2 = -ic\boldsymbol{\alpha}\cdot\nabla + \beta mc^2}$$

$\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \alpha_3)$ and β are 4×4 self-adjoint matrices satisfying the CAR

$$\alpha_i\alpha_j + \alpha_j\alpha_i = 2\delta_{ij}, \qquad \alpha_i\beta + \beta\alpha_i = 0.$$

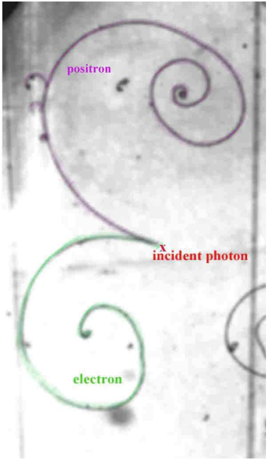
D^0 is defined on $L^2(\mathbb{R}^3, \mathbb{C}^4)$ with domain $H^1(\mathbb{R}^3, \mathbb{C}^4)$ and

$$(D^0)^2 = -c^2\Delta + m^2c^4.$$

It is *unbounded from below*:

$$\sigma(D^0) = (-\infty; -mc^2] \cup [mc^2; +\infty).$$

Dirac's interpretation of the negative continuous spectrum



Spontaneaous creation of an electron-positron pair.
Source: `www.cern.ch`

Dirac (1934): *"We make the assumption that, in the world as we know it, nearly all the states of negative energy for the electrons are occupied, with just one electron in each state, and that a uniform filling of all the negative-energy states is completely unobservable to us."*

$\rightarrow$ **Vacuum = Dirac sea** = infinitely many virtual electrons occupying the negative energies.

- can feel an external field and will react accordingly $\rightarrow$ **Vacuum Polarization.**
- if the external field is strong enough, **electron-positron pairs** can be created.

Consequence: real electrons can only occupy positive energy states.

Hartree-Fock states

- **State of the system** = an orthogonal projector P acting on $L^2(\mathbb{R}^3, \mathbb{C}^4)$.
  - Rank(P) = infinite number of particles (virtual and "real" electrons);
  - if $(\varphi_i)_{i \in I}$ is an orthonormal basis of Ran(P), $P = \sum_{i \in I} |\varphi_i\rangle\langle\varphi_i|$, then φ_i's = states of the individual electrons.

Examples. Introduce $P^0 = P^0_- = \chi_{(-\infty;0)}(D^0)$ and $P^0_+ = 1 - P^0$. Let $(\varphi_i^\pm)_i$ be an orthonormal basis of $\mathfrak{H}^0_\pm := P^0_\pm L^2(\mathbb{R}^3, \mathbb{C}^4)$.

Free Dirac sea	**An electron-positron pair**
$P = P^0_- = \sum_{i=1}^\infty |\varphi_i^-\rangle\langle\varphi_i^-|$	$P = P^0_- - |\varphi_1^-\rangle\langle\varphi_1^-| + |\varphi_1^+\rangle\langle\varphi_1^+|$
$Q = P - P^0_- = 0$	$Q = -|\varphi_1^-\rangle\langle\varphi_1^-| + |\varphi_1^+\rangle\langle\varphi_1^+|$.

- **Units in the sequel:** $\hbar = m = c = 1$, $\alpha = e^2$ (fine structure cst).

Hartree-Fock (formal) energy

- **Formal Energy in the state** P: $\mathcal{E}^{\nu}_{\rm HF}(P-1/2)+\mathrm{Cst}$,

$$\mathcal{E}^{\nu}_{\rm HF}(\Gamma)=\mathrm{tr}(D^0\Gamma)-\alpha\iint\frac{\nu(x)\rho_\Gamma(y)}{|x-y|}dx\,dy \\ +\frac{\alpha}{2}\iint\frac{\rho_\Gamma(x)\rho_\Gamma(y)}{|x-y|}dx\,dy-\frac{\alpha}{2}\iint\frac{|\Gamma(x,y)|^2}{|x-y|}dx\,dy,$$

Here: $\rho_\Gamma(x)=\mathrm{tr}_{\mathbb{C}^4}(\Gamma(x,x))$.
Last term: non-convex *"exchange term"* $\rightarrow$ neglected in this talk !

$$\mathcal{E}^{\nu}_{\rm rHF}(P-1/2)=\mathrm{tr}(D^0(P-1/2))-\alpha\iint\frac{\nu(x)\rho_{P-1/2}(y)}{|x-y|}dx\,dy \\ +\frac{\alpha}{2}\iint\frac{\rho_{P-1/2}(x)\rho_{P-1/2}(y)}{|x-y|}dx\,dy,$$

Not well-defined: in infinite dimension, $P-1/2$ is never compact !

The Free Vacuum ($\nu = 0$)

$$\mathcal{E}^0_{\mathrm{rHF}}(P - 1/2) = \mathrm{tr}(D^0(P - 1/2)) + \frac{\alpha}{2} \iint \frac{\rho_{P-1/2}(x)\rho_{P-1/2}(y)}{|x-y|} dx\, dy$$

Free vacuum: the ground state is (formally) $\boxed{P = P^0_- = \chi_{(-\infty,0]}(D^0)}$

$\rightarrow$ Dirac's picture of the vacuum.

$$P^0_- - \frac{1}{2} = -\frac{\mathrm{sgn}(D^0)}{2} \Rightarrow \left(P^0_- - \frac{1}{2}\right)(x,y) = (2\pi)^{-3/2} \check{f}(x-y)$$

where $f(p) = -\frac{D^0(p)}{2|D^0(p)|} = -\frac{\boldsymbol{\alpha}\cdot p + \beta}{2\sqrt{1+|p|^2}}$. Hence (formally)

$$\rho_{P^0_- -1/2}(x) = (2\pi)^{-3/2}\, \mathrm{tr}_{\mathbb{C}^4}(\check{f}(0)) = (2\pi)^{-3} \int \mathrm{tr}_{\mathbb{C}^4}(f(p))\, dp \equiv 0.$$

The (reduced) Bogoliubov-Dirac-Fock Energy

Idea: subtract the (infinite) energy of the free vacuum:

$$\begin{aligned}\mathcal{E}^\nu(P - P^0_-) &:= \text{“}\mathcal{E}^\nu_{\rm rHF}(P - 1/2) - \mathcal{E}^0_{\rm rHF}(P^0_- - 1/2)\text{”} \\ &= \mathrm{tr}(D^0(P - P^0_-)) - \alpha \iint \frac{\rho_{P-P^0_-}(x)\nu(y)}{|x-y|}\,dx\,dy \\ &\qquad + \frac{\alpha}{2}\iint \frac{\rho_{P-P^0_-}(x)\rho_{P-P^0_-}(y)}{|x-y|}\,dx\,dy\end{aligned}$$

Rmk. this model can be justified by a thermodynamic limit (Hainzl-Lewin-Solovej, *CMP* '06).

Rmk. With exchange term, $\mathcal{E}^\nu$ was introduced by Chaix-Iracane (*J. Phys. B* '89) and mathematically studied by Bach-Barbaroux-Helffer-Siedentop (*CMP* '99) for $\nu = 0$. Then Hainzl-Lewin-S. (*CMP* '05, *J. Phys. A* '05) for $\nu \neq 0$.

A well-defined model (Hainzl-Lewin-S. '05)

Pb: A minimizer $P - P^0$ of $\mathcal{E}^\nu$ *will not* be trace class when $\nu \neq 0$. The expression $\rho_\Gamma(x)$ is not well defined.

Solution:

-We add an ultraviolet cut-off and work in the Hilbert space

$$\mathfrak{H}_\Lambda = \{f \in L^2(\mathbb{R}^3; \mathbb{C}^4),\ \mathrm{supp}(\widehat{f}) \subset B(0;\Lambda)\}.$$

-We introduce a new class of operators on this space: a Hilbert-Schmidt operator $\Gamma \in \mathfrak{S}_2(\mathfrak{H}_\Lambda)$ is P^0-trace class ($\Gamma \in \mathfrak{S}_1^{P^0}(\mathfrak{H}_\Lambda)$) if $\Gamma^{++} := P^0_+ \Gamma P^0_+$ and $\Gamma^{--} := P^0 \Gamma P^0$ are trace-class. We then define its P^0-trace as $\mathrm{tr}_{P^0}(\Gamma) := \mathrm{tr}(\Gamma^{++} + \Gamma^{--})$.

-The density $\rho_Q(x) = \mathrm{tr}_{\mathbb{C}^4}(Q(x,x))$ is well-defined $\forall Q \in \mathfrak{S}_2(\mathfrak{H}_\Lambda)$ since $\mathrm{Supp}\ \widehat{Q} \subseteq B(0,\Lambda)^2 \Rightarrow Q(x,y)$ smooth. We introduce:

$$D(f,g) := 4\pi \int_{\mathbb{R}^3} |k|^{-2} \overline{\widehat{f}(k)} \widehat{g}(k), \qquad \mathcal{C} := \{f \mid D(f,f) < \infty\}.$$

Definition of the BDF Energy

$$\boxed{\mathcal{E}^{\nu}(Q) := \mathrm{tr}_{P^0_-}(D^0 Q) - \alpha D(\nu, \rho_Q) + \frac{\alpha}{2} D(\rho_Q, \rho_Q)}$$

$$Q \in \mathcal{Q}_\Lambda := \left\{ Q \in \mathfrak{S}_1^{P^0_-}(\mathfrak{H}_\Lambda) \mid Q^* = Q,\ -P^0_- \leq Q \leq P^0_+ \right\}.$$

(Convex hull of $\{Q = P - P^0_- \in \mathfrak{S}_2(\mathfrak{H}_\Lambda)\}$, cf Lieb, PRL '81)

Lemma (The BDF Energy is bounded-below)

$\alpha \geq 0$, $\Lambda > 0$, $\nu \in \mathcal{C}$. *The functional* $\mathcal{E}^\nu$ *is well-defined on* $\mathcal{Q}_\Lambda$. *It satisfies*

$$\forall Q \in \mathcal{Q}_\Lambda, \qquad \mathcal{E}^\nu(Q) + \frac{\alpha}{2} D(\nu, \nu) \geq 0$$

and it is thus bounded-below. If moreover $\nu = 0$, *then* $\mathcal{E}^0$ *is nonnegative, 0 being its unique minimizer.*

Proof: Notice $-P^0_- \leq Q \leq P^0_+ \iff Q^2 \leq Q^{++} - Q^{--}$ and $\mathrm{tr}_{P^0_-}(D^0 Q) = \mathrm{tr}(|D^0|(Q^{++} - Q^{--})) \geq \mathrm{tr}(Q^{++} - Q^{--}) \geq \mathrm{tr}(Q^2) \geq 0$.

Existence of solutions

$$\begin{cases} P = \chi_{(-\infty,\mu)}(D) + \delta\,, \quad 0 \le \delta \le \chi_{\{\mu\}}(D) \\ D = \Pi_\Lambda \left(D^0 + \alpha(\rho_{P-P^0_-} - \nu) * \frac{1}{|x|} \right) \Pi_\Lambda \end{cases} \tag{1}$$

Theorem (Existence of solutions for $\Lambda < \infty$)

Let $\mu \in (-1,1)$, $\alpha \ge 0$, $\Lambda > 0$ and $\nu \in \mathcal{C}$.

(i) There exists **at least one solution** *to (1) s.t. $Q = P - P^0_- \in \mathcal{Q}_\Lambda$.*

(ii) The solutions of (1) are exactly the minimizers of the rBDF energy with chemical potential μ

$$Q \mapsto \mathcal{E}^\nu(Q) - \mu\, \mathrm{tr}_{P^0_-}(Q)\,.$$

The corresponding density $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$ is **unique**.

(iii) If $\alpha\pi^{1/6}2^{11/6}\,\|\nu\|_{\mathcal{C}} < 1$ and $\mu = 0$, then $\ker(D) = \{0\}$, hence $\delta = 0$ and $P = P^2$ is unique. In this case $\mathrm{tr}_{P^0_-}(P - P^0_-) = 0$.

[HaiLewSer05b] C. Hainzl, M.Lewin and É. S. *J. Phys. A: Math & Gen.*, 2005.

Property of solutions and renormalized charge

Theorem (L^1 regularity and renormalization [GraLewSer09])

Let $\alpha \geq 0$, $\Lambda > 0$, $\mu \in (-1,1)$ *and* $\nu \in \mathcal{C} \cap L^1(\mathbb{R}^3)$ *with* $Z = \int_{\mathbb{R}^3} \nu$. *Let* P *be a solution of* (1) *with* $P - P^0_- \in \mathcal{Q}_\Lambda$. *Then* $\rho_{P-P^0_-} \in L^1(\mathbb{R}^3)$ *and*

$$Z - \int_{\mathbb{R}^3} \rho_{P-P^0_-} = \frac{Z - \mathrm{tr}_{P^0_-}(P - P^0_-)}{1 + \alpha B_\Lambda} \qquad (2)$$

where $B_\Lambda = \frac{2}{3\pi} \log \Lambda - \frac{5}{9\pi} + \frac{2 \log 2}{3\pi} + O(1/\Lambda^2)$.

• **Physical charge.** If $\alpha \pi^{1/6} 2^{11/6} D(\nu,\nu)^{1/2} < 1$, then $\mathrm{tr}_{P^0_-}(P - P^0_-) = 0$ but $\int \rho_{P-P^0_-} \neq 0$. Potential observed far away: $\alpha_{\rm phys} Z/|x|$ where

$$\alpha_{\rm ph} = \frac{\alpha}{1 + \alpha B_\Lambda} \iff \alpha = \frac{\alpha_{\rm ph}}{1 - \alpha_{\rm ph} B_\Lambda}.$$

Note one always has $\alpha_{\rm ph} B_\Lambda < 1$ (Landau pole).

[GraLewSer09] P. Gravejat, M.Lewin & É. S. *Commun. Math. Phys.*, 2009.

Self-consistent equation

- Assume for simplicity $\mu = 0$ and $\ker(D) = \{0\}$. From Cauchy's formula

$$P - P^0_- = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\eta \left(\frac{1}{D+i\eta} - \frac{1}{D^0+i\eta}\right),$$

we get in Fourier space

$$\widehat{\rho}_{P-P^0_-}(k) = -\alpha B_\Lambda(k)\big(\widehat{\rho}_{P-P^0_-}(k) - \widehat{\nu}(k)\big) + \widehat{F}_\Lambda\big(\alpha(\rho_{P-P^0_-} - \nu)\big) \qquad (3)$$

where

$$B_\Lambda(k) = -\frac{1}{\pi^2|k|^2}\int_{\substack{|\ell+k/2|\leq\Lambda,\\ |\ell-k/2|\leq\Lambda}} \frac{(\ell+k/2)\cdot(\ell-k/2)+1-E(\ell+k/2)E(\ell-k/2)}{E(\ell+k/2)E(\ell-k/2)(E(\ell+k/2)+E(\ell-k/2))}\,d\ell$$

and $F_\Lambda(f) = \sum_{n\geq 1} F_{2n+1,\Lambda}(f,\dots,f)$ with

$$F_{k,\Lambda}(f_1,\dots,f_k) = \rho\left[\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{1}{D^0+i\eta}\prod_{j=1}^{k}\left(\Pi_\Lambda f_j * \frac{1}{|x|}\Pi_\Lambda \frac{1}{D^0+i\eta}\right)d\eta\right].$$

- **Note:** $B_\Lambda = B_\Lambda(0) = 2/(3\pi)\log\Lambda - 5/(9\pi) + 2\log 2/(3\pi) + O(1/\Lambda^2)$.

Renormalized equation

- Define for convenience $\rho_{\rm ph} = \rho_{\rm ph}(\alpha_{\rm ph}, \Lambda)$ by (for $\alpha_{\rm ph} B_\Lambda < 1$)

$$\alpha(\nu - \rho_{P-P^0_-}) = \alpha_{\rm ph}\rho_{\rm ph}$$

such that $D = D^0 - \alpha_{\rm ph}\rho_{\rm ph} * |\cdot|^{-1}$.

- We can re-express Eq. (3) in terms of physical quantities as

$$(1 - \alpha_{\rm ph} U_\Lambda(k))\widehat{\rho}_{\rm ph} + \widehat{F}_\Lambda(\alpha_{\rm ph}\rho_{\rm ph}) = \widehat{\nu}$$

where $U_\Lambda(k) = B_\Lambda(0) - B_\Lambda(k) \geq 0$.

Rmk.

$$\lim_{\Lambda\to\infty} U_\Lambda(k) = \frac{|k|^2}{4\pi}\int_0^1 \frac{z^2 - z^4/3}{1+|k|^2(1-z^2)/4}dz := U(k) \sim_{|k|\to\infty} \frac{2}{3\pi}\log|k|.$$

[HaiLewSer05b] C. Hainzl, M.Lewin and É. S. *J. Phys. A: Math & Gen.*, 2005.
[Ueh35] E.A. Uehling. *Phys. Rev.*, 1935.

Renormalization in perturbation theory

- At least formally, we can write

$$\rho_{\rm ph}(\alpha_{\rm ph},\Lambda)=\sum_{n\geq 0}(\alpha_{\rm ph})^n\nu_{n,\Lambda}$$

where
$$\begin{cases} \widehat{\nu}_{0,\Lambda}=\widehat{\nu}\mathbb{1}_{B(0,2\Lambda)}, \quad \widehat{\nu}_{1,\Lambda}=U_\Lambda(k)\widehat{\nu}_0(k), \\ \widehat{\nu}_{n,\Lambda}=U_\Lambda\widehat{\nu}_{n-1,\Lambda}+\displaystyle\sum_{j=3}^{n}\sum_{n_1+\cdots+n_j=n-j}\widehat{F}_{j,\Lambda}\left(\nu_{n_1,\Lambda},\ldots,\nu_{n_j,\Lambda}\right) \text{ for } n\geq 2. \end{cases}$$

- Limit $\Lambda\to\infty$ in above recursion formula $\Rightarrow$ a sequence $\{\nu_n\}_{n\geq 0}$ (for ν smooth enough). Note $\nu_0=\nu$ and

$$\nu_1*\frac{1}{|x|}=\frac{1}{3\pi}\int_1^\infty dt\,(t^2-1)^{1/2}\left[\frac{2}{t^2}+\frac{1}{t^4}\right]\int_{\mathbb{R}^3}e^{-2|x-y|t}\frac{\nu(y)}{|x-y|}\,dy$$

is the **Uehling potential**.

Question: what can one say about the series $\sum_{n\geq 0}(\alpha_{\rm ph})^n\nu_n$?
Dyson ('52): the series is expected to **diverge**.

[Dys52] F.J. Dyson. *Phys. Rev.*, 1952.

Asymptotics as $\alpha_{\rm ph} \longrightarrow 0$

$\rho_{\rm ph}(\alpha_{\rm ph}, \Lambda)$ is, perturbatively, essentially independent of Λ:

Theorem (Asymptotics as $\alpha_{\rm ph} \longrightarrow 0$ [GraLewSer])

Let $\mu = 0$ and $\nu \in L^2(\mathbb{R}^3) \cap \mathcal{C}$ such that, for some $m \geq 1$,

$$\int_{\mathbb{R}^3} \log(1 + |k|)^{2m+4} |\widehat{\nu}(k)|^2 \, dk < \infty.$$

Let $\epsilon > 0$. There exist two constants $C(\nu, m, \epsilon)$ and $a(\nu, m, \epsilon)$ depending on m, ν and ϵ such that one has

$$\left\| \rho_{\rm ph}(\alpha_{\rm ph}, \Lambda) - \sum_{n=0}^{m} (\alpha_{\rm ph})^n \nu_n \right\|_{L^2(\mathbb{R}^3) \cap \mathcal{C}} \leq C(\nu, m, \epsilon) \, (\alpha_{\rm ph})^{m+1} \qquad (4)$$

for all $0 \leq \alpha_{\rm ph} \leq a(\nu, m, \epsilon)$ with $\epsilon \leq \alpha_{\rm ph} B_\Lambda \leq 1 - \epsilon$.

Rmk. We take essentially $\Lambda \sim e^{\frac{3\kappa\pi}{2\alpha_{\rm ph}}}$ with $0 < \epsilon \leq \kappa \leq 1 - \epsilon$.

[GraLewSer] P. Gravejat, M.Lewin and É. S. In preparation.