Relativistic electrons coupled with Newtonian nuclear dynamics

Workshop on Model Systems in Quantum Mechanics

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12 January 2024

Introduction

Nonrelativistic: well-known $N-$body Schrödinger theory

$$H = -\sum_{k=1}^{M} \frac{1}{2m_k} \Delta_{\overline{x}_k} - \sum_{i=1}^{J} \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^{J} \sum_{k=1}^{M} \frac{z_k}{|x_i - \overline{x}_k|} + \sum_{1 \le i < j \le J} \frac{1}{|x_i - x_j|} + \sum_{1 \le k < l \le M} \frac{z_k z_l}{|\overline{x}_k - \overline{x}_l|},$$

(M nuclei of mass m_k and charge z_k, J electrons of unitary mass and charge).

Atoms with heavy nuclei (Au: $Z = 79$) $\rightarrow$ **non-negligible relativistic effects** ($v_{electron} \approx \frac{Zc}{137}$).

The Dirac operator

Relativistic motion of spin-1/2 particles (electrons):

$$D^0 = -ic\boldsymbol{\alpha} \cdot \nabla + \beta mc^2,$$

where (standard representation in $\mathbb{C}^4$)

$$\beta = \begin{bmatrix} \mathbb{1}_{\mathbb{C}^2} & 0 \\ 0 & -\mathbb{1}_{\mathbb{C}^2} \end{bmatrix}, \quad \alpha_i = \begin{bmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{bmatrix}, \quad i = 1, 2, 3,$$

with σ_i, $i = 1, 2, 3$, Pauli matrices.

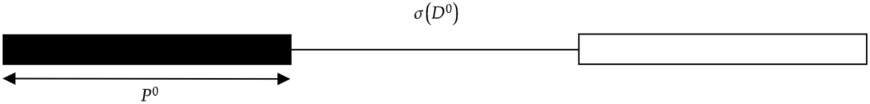
Derivation = energy-momentum relation $E^2 = m^2 p^2 + m^2 c^4$ + linearisation + first quantisation.

The spectrum of D^0

$$\boxed{\sigma\left(D^0\right) = \left(-\infty, -mc^2\right] \cup \left[mc^2, +\infty\right)}$$

Consequences:

- Negative energy states = virtual electrons $\rightarrow$ **Dirac sea** $P^0 = \mathbb{1}_{(-\infty,0)}\left(D^0\right)$.



- No equivalent of $N-$body Schrödinger theory involving D^0 (recall $\sigma\left(-\Delta\right) = [0, +\infty)$ on $\mathbb{R}^3$).
- Inconsistencies in Dirac(-Hartree)-Fock model: ground state $\neq$ minimiser of physical energy.

$\ldots \implies$ **Quantum electrodynamics** = matter (charged particles) and light (photons) interaction (special relativity + QM).

QED = perturbation theory $\rightarrow$ restricted range of applications.
Nonperturbative physical situations:

- Heavy atoms (strong electric field) $\leftarrow$ our starting example!
- Neutron stars (strong magnetic field).

$\implies$ **Bogoliubov-Dirac-Fock model**: nonperturbative mean-field approximation of QED.

The Bogoliubov-Dirac-Fock model

No photons QED Hamiltonian in Coulomb gauge (second quantisation):

$$\mathbb{H}^{\varphi} = \int \Psi^{*}(x) D^{0} \Psi(x)\, dx - \int \varphi(x) \rho(x)\, dx + \frac{\alpha}{2} \int \int \frac{\rho(x)\rho(y)}{|x-y|} dxdy^{1}.$$

1. Compute an energy functional by means of an **Hartree-Fock approximation:**

$$\mathcal{E}_{\mathrm{HF}}^{\varphi}(P) = \langle \Omega_P, \mathbb{H}^{\varphi} \Omega_P \rangle,$$

   where Ω_P is an "infinite Slater determinant" corresponding to an orthogonal projection P on $L^2(\mathbb{R}^3, \mathbb{C}^2)$.

[1] Field operator Ψ, density operator ρ, external potential φ, Sommerfeld constant α.

The Bogololiubov-Dirac-Fock model

2. Take the (infinite) energy of the **free vacuum as a reference:**

$$\mathcal{E}^{\varphi}_{\mathrm{BDF}}(Q) = \mathcal{E}^{\varphi}_{\mathrm{HF}}(P) - \mathcal{E}^{0}_{\mathrm{HF}}\left(P^0\right).$$

3. Define P^0-**trace class**[2] and add an **ultraviolet cutoff** $\Lambda > 0$ (operator space $\mathcal{H}_\Lambda$[3]) to get a well defined energy functional:

$$\mathcal{E}^{\varphi}_{\mathrm{BDF}}(Q) = \mathrm{Tr}_{P^0}\left(D^0 Q\right) - \alpha \int_{\mathbb{R}^3} \rho_Q(x)\,\varphi(x)\,dx + \frac{\alpha}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho_Q(x)\,\rho_Q(y)}{|x-y|}\,dxdy - \frac{\alpha}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|Q(x,y)|^2}{|x-y|}\,dxdy.$$

[2] $\mathrm{Tr}_{P^0}(A) = \mathrm{Tr}\left(P^0 A P^0\right) + \mathrm{Tr}\left(\left(1-P^0\right) A \left(1-P^0\right)\right)$

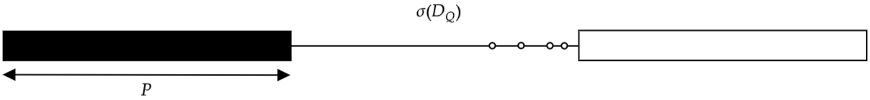
[3] $\mathcal{H}_\Lambda = \left\{Q \in \mathfrak{S}_2\left(\mathfrak{H}_\Lambda\right);\ \rho_Q \in \mathcal{C}\right\}$ where $\mathfrak{H}_\Lambda = \left\{f \in L^2\left(\mathbb{R}^3, \mathbb{C}^4\right);\ \widehat{f} \subseteq B(0,\Lambda)\right\}$

The BDF evolution equation

Energy functional $\mathcal{E}^{\varphi}_{BDF} \to$ Euler-Lagrange equation:

- Stationary: $[D_Q, P] = 0$.
- Nonstationary: $\boxed{i\frac{d}{dt}P = [D_Q, P]} \leftarrow$ Von Neumann equation.

with $D_Q := \mathcal{P}_\Lambda \left(D^0 - \alpha\varphi + \alpha\rho_Q * \frac{1}{|\cdot|} - \alpha\frac{Q(x,y)}{|x-y|} \right) \mathcal{P}_\Lambda$[4] (**mean-field operator**).



[4]Orthogonal projection $\mathcal{P}_\Lambda$ of $L^2(\mathbb{R}^3)$ onto $\mathfrak{H}_\Lambda$

Coupling with Newtonian nuclear dynamics

- M classical nuclei ($m_{\mathrm{nucleon}} \approx 1836\, m_{\mathrm{electron}}$): charges z_k, masses m_k, and centers of mass $\overline{x}_k$, $k = 1, \ldots, M$.
- Normalised nuclei charge distributions f_k such that $\varphi_k = f_k\left(|\cdot - \overline{x}_k|\right) * |\cdot|^{-1}$ are the associated potentials.
- Nucleus-electron interactions (Coulomb space $\mathcal{C} = \dot{H}^{-1}$) + nucleus-nucleus interactions:

$$W_Q\left(t, \overline{x}_1, \ldots, \overline{x}_M\right) = \alpha \sum_{i=1}^{M} \int_{\mathbb{R}^3} \frac{\overline{\widehat{\rho}_{Q(t)}(k)} z_i \widehat{f_i\left(|\cdot - \overline{x}_i|\right)}(k)}{|k|^2} dk - \alpha \sum_{1 \leq i < j \leq M} \int \int \frac{z_i f_i\left(|x - \overline{x}_i|\right) z_j f_j\left(|y - \overline{x}_j|\right)}{|x - y|} dx dy$$

Coupling with Newtonian nuclear dynamics

- Coupled equations + Cauchy data:

$$\boxed{\begin{cases} i\frac{d}{dt}P(t) = [D_{Q,\overline{x}_1,\ldots,\overline{x}_M}, P(t)], \\ m_k\frac{d^2}{dt^2}\overline{x}_k(t) = -\nabla_{\overline{x}_k}W_Q(t,\overline{x}_1,\ldots,\overline{x}_M), \quad k=1,\ldots M, \\ P(0)=P_I,\ P(t)^2=P(t),\ Q(t)=P(t)-P(0)\in\mathcal{H}_\Lambda, \\ \overline{x}_k(0)=\overline{x}_k^0\in\mathbb{R}^3,\ \frac{d\overline{x}_k}{dt}(0)=\overline{v}_k^0\in\mathbb{R}^3, \quad k=1,\ldots M, \end{cases}} \qquad (\Sigma)$$

- Total energy of the system:

$$E^{(M)}(Q(t),\overline{x}_1(t),\ldots,\overline{x}_M(t)) = \mathcal{E}^{\varphi}_{\mathrm{BDF}}(Q(t)) + \frac{1}{2}\sum_{k=1}^{M} m_k\left|\dot{\overline{x}}_k(t)\right|^2 + \alpha\sum_{1\leq i<j\leq M}\int\int\frac{z_i f_i(|x-\overline{x}_i(t)|)\, z_j f_j(|y-\overline{x}_j(t)|)}{|x-y|}dxdy.$$

Main result

Theorem (U.M. 2023)

Let $0 \leq \alpha < 4/\pi$ and $f_k \in L^1(\mathbb{R}^3) \cap L^2(\mathbb{R}^3) \cap \mathcal{C}$, $k = 1, \dots M$. Let P_I be an orthogonal projector such that $Q_I = P_I - P^0 \in \mathcal{H}_\Lambda$ and $\overline{x}_k^0, \overline{v}_k^0 \in \mathbb{R}^3$, $k = 1, \dots M$. Then there exists a unique global solution

$$(Q, \overline{x}_1, \dots, \overline{x}_M) \in C^1([0, +\infty), \mathcal{H}_\Lambda) \times \left(C^2([0, +\infty), \mathbb{R}^3)\right)^M$$

of system (Σ). Moreover, $Q(t) = P(t) - P^0$ is P^0-trace class and

$$\mathrm{tr}_{P^0}(Q(t)) = \mathrm{tr}_{P^0}(Q_I)$$

and

$$E^{(M)}(Q(t), \overline{x}_1(t), \dots, \overline{x}_M(t)) = E^{(M)}(Q_I, \overline{x}_1^0, \dots, \overline{x}_M^0),$$

for all $t \in [0, +\infty)$.

Don't hesitate to ask me for the PROOF!

Thanks for your attention!

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement N°945332.

Bonus track: proof step by step

1. **Local existence:**
   - Decouple the two equations and solve them separately (existence and uniqueness theorem for ODEs).
   - Apply a fixed-point argument (Schauder fixed-point theorem).
     Consequence: $P(t)$ is an orthogonal projector and then $Q(t)$ is P^0-trace class with $\mathrm{Tr}_{P^0}(Q(t))$ constant along the time evolution.
2. **Uniqueness:**
   - Apply Grönwall's lemma.
3. **Global existence:**
   - Prove that the energy is conserved along any solution.
   - Show the boundedness of the solution by means of the conservation of energy and Kato's inequality.
     Consequence: No finite time blow-up $\implies$ the solution is global.