Real space quantum mechanics

An application to atoms and a discussion for the relativistic extension

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Dr Ophelliam Loiselet (R&d manufacturing engineer, Alten SA)
oplslt@mail.com

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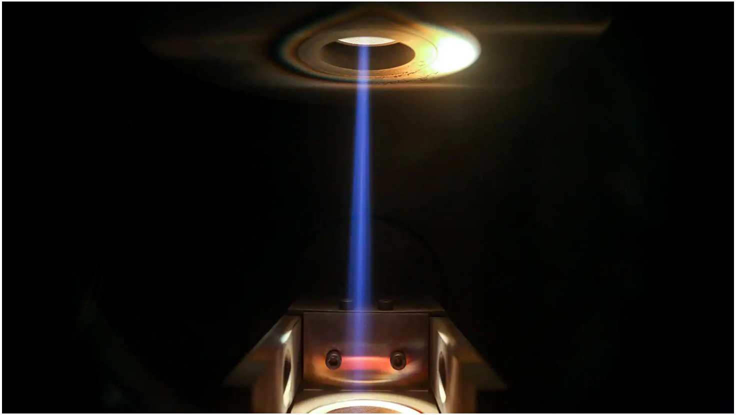
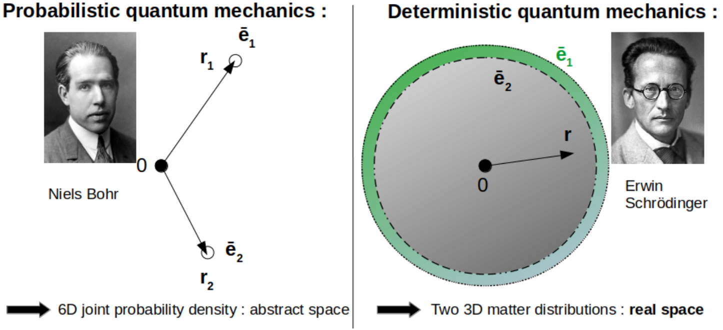
An electron beam as an introduction



- An electron gun releases electrons in a chamber
- The electron beam excites gas particles
- The excited particles release photons
- We see the photons with our eyes : **a real phenomena in the real space**

Deterministic vs probabilistic conception of quantum mechanics



- Bohr's interpretation : $|\Phi(\boldsymbol{r_1}, \boldsymbol{r_2})|^2$ **joint probability density** of the electron 1 to be at $\boldsymbol{r_1}$ and electron 2 to be at $\boldsymbol{r_2}$
- Schrödinger's original idea : $|\Phi_1(\boldsymbol{r})|^2$ and $|\Phi_2(\boldsymbol{r})|^2$ **matter distribution** of electron 1 and electron 2 at $\boldsymbol{r}$ $\Rightarrow$ like "mini-clouds"

Why real space quantum mechanics?

Issues with Bohr's model :

- Probabilistic **abstract** sub-spaces
- **Not relativistic** for two and more electrons, **mismatch** with general relativity
- Many **paradoxes** (particle-wave duality, "location" ...)
- Measurement problems, difficulty of interpretations ...

Advantages of Schrödinger's model :

- Inside the **Real** 3D space
- **Can be relativistic** (extension of Dirac equation), **compatible** with general relativity (Arminjon [1])
- The electron is a **matter-wave**, like an oscillating cloud
- Maybe an **alternative** way to explain measurements and other problems in QM

Purpose of the topic $\Rightarrow$ derive a relativistic equation for N-electrons atom in real space

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One electron atom : Schrödinger equation, 1926

Schrödinger/De Broglie theory :

- Hydrogen atom : electron is a **stationary wave** described by $\Psi(\boldsymbol{r},t) = \Phi(\boldsymbol{r})e^{-iEt/\hbar}$
- $|\Psi(\boldsymbol{r},t)|^2$ is the **electron matter density**, i.e $\int d^3r|\Psi|^2 = 1$
- **Schrödinger equation** for hydrogen :

$$-\left(\frac{\Delta}{2} + \frac{1}{r}\right)\Psi(\boldsymbol{r},t) = i\hbar\partial_t\Psi(\boldsymbol{r},t) \quad (1)$$

Two and more electrons atoms : Solvay conf. 1927

⇒ The **probabilistic interpretation is retained** at the conference

- N electrons atom → described in **3N-D probabilistic space** wave function $\Phi(\boldsymbol{r_1}, ..., \boldsymbol{r_N})$
- Definition of the **N-electrons Hamiltonian** H (∼ fixed nucleus) :

$$H = -\sum_{i=1}^{N} \left(\frac{\Delta_{\boldsymbol{r_i}}}{2} + \frac{Z}{r_i} \right) + \sum_{i \neq j} \frac{1}{\|\boldsymbol{r_i} - \boldsymbol{r_j}\|} \qquad (2)$$

- Eigenvalue equation :

$$H\Phi(\boldsymbol{r_1}, ..., \boldsymbol{r_N}) = E\Phi(\boldsymbol{r_1}, ..., \boldsymbol{r_N})$$

with E the total energy of the electrons and the probability condition :

$$\int d^3 r_1 ... \int d^3 r_N |\Phi(\boldsymbol{r_1}, ..., \boldsymbol{r_N})|^2 = 1$$

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Hartree approximation, 1927

Multi-electronic wave function can be **approximated** by :

$$\Phi(\boldsymbol{r_1}, \dots, \boldsymbol{r_N}) \simeq \Phi_1(\boldsymbol{r_1}) \dots \Phi_N(\boldsymbol{r_N}) \tag{3}$$

That gives for each wave function Φ_i ($\int d^3 r_1 |\Phi_i(\boldsymbol{r_i})|^2 = 1$) an **Hartree equation** ($E = \sum_i E_i$)) :

$$\left[-\frac{\Delta_{\boldsymbol{r_i}}}{2} - \frac{Z}{r_i} + \frac{1}{2} \sum_{j \neq i} \int d^3 r_j \frac{|\Phi_j(\boldsymbol{r_j})|^2}{\|\boldsymbol{r_i} - \boldsymbol{r_j}\|} \right] \Phi_i(\boldsymbol{r_i}) \simeq E_i \Phi_i(\boldsymbol{r_i}) \tag{4}$$

Which is a **3D equation** ($\boldsymbol{r_i} \to \boldsymbol{r}$, $\boldsymbol{r_j} \to \boldsymbol{r'}$) (Simons [2]) :

$$\left[-\frac{\Delta}{2} - \frac{Z}{r} + \frac{1}{2} \sum_{j \neq i} \int d^3 r' \frac{|\Phi_j(\boldsymbol{r'})|^2}{\|\boldsymbol{r} - \boldsymbol{r'}\|} \right] \Phi_i(\boldsymbol{r}) \simeq E_i \Phi_i(\boldsymbol{r}) \tag{5}$$

$\to$ we **came back in real space**! But energy is **too high** $\to$ we need other terms to lower E (exchange energy)...

Hartree-Fock approximation, 1928

In the Hartree-Fock approximation (using Pauli exclusion principle) the wave function become a (single) Slater determinant :

$$\Phi(\boldsymbol{r_1}, ..., \boldsymbol{r_N}) \simeq \frac{1}{\sqrt{N!}} \begin{vmatrix} \Phi_1(\boldsymbol{r_1})\chi_1 & \Phi_2(\boldsymbol{r_1})\chi_2 & ... & \Phi_N(\boldsymbol{r_1})\chi_N \\ \Phi_1(\boldsymbol{r_2})\chi_1 & \Phi_2(\boldsymbol{r_2})\chi_2 & ... & \Phi_N(\boldsymbol{r_2})\chi_N \\ ... & ... & ... & ... \\ \Phi_1(\boldsymbol{r_N})\chi_1 & \Phi_2(\boldsymbol{r_N})\chi_2 & ... & \Phi_N(\boldsymbol{r_N})\chi_N \end{vmatrix} \tag{6}$$

$\rightarrow$ using Slater-Condon rules the eigenvalue equation become :

$$\left[-\frac{\Delta_{\boldsymbol{r_i}}}{2} - \frac{Z}{r_i} + \frac{1}{2} \sum_{j \neq i} \int d^3 r_j \frac{|\Phi_j(\boldsymbol{r_j})|^2}{\|\boldsymbol{r_i} - \boldsymbol{r_j}\|} \right] \Phi_i(\boldsymbol{r_i}) + \sum_{j \neq i} v_{i,j}(\boldsymbol{r_i}) \Phi_j(\boldsymbol{r_i}) \simeq E_i \Phi_i(\boldsymbol{r_i}) \tag{7}$$

with the appearance of the (**sill unclear**) exchange potential :

$$v_{i,j}(\boldsymbol{r_i}) = -\frac{1}{2} \int d^3 r_j \frac{\Phi_i(\boldsymbol{r_j}) \Phi_j^*(\boldsymbol{r_j})}{\|\boldsymbol{r_i} - \boldsymbol{r_j}\|} \delta_{s_i, s_j} \tag{8}$$

Hartree-Fock approximation... also a 3D equation

Eq. (7) is still equivalent to a **3D equation** ($\boldsymbol{r_i} \to \boldsymbol{r}$, $\boldsymbol{r_j} \to \boldsymbol{r'}$) [2] :

$$\left[-\frac{\Delta}{2} - \frac{Z}{r} + \frac{1}{2}\sum_{j\neq i}\int d^3r' \frac{|\Phi_j(\boldsymbol{r'})|^2}{\|\boldsymbol{r}-\boldsymbol{r'}\|}\right]\Phi_i(\boldsymbol{r}) + \sum_{j\neq i} v_{i,j}(\boldsymbol{r})\Phi_j(\boldsymbol{r}) \simeq E_i\Phi_i(\boldsymbol{r}) \tag{9}$$

Hartree-Fock theory is **already in real space** ! With the exchange term :

$$v_{i,j}(\boldsymbol{r}) = -\frac{1}{2}\int d^3r' \frac{\Phi_i(\boldsymbol{r'})\Phi_j^*(\boldsymbol{r'})}{\|\boldsymbol{r}-\boldsymbol{r'}\|}\delta_{s_i,s_j} \tag{10}$$

$\Rightarrow$ This could be extended in **non-stationary form** (part 4)...

We make a break and remark an **unusual quantity** : the (Schrödinger) **cross charge density** $\Phi_i\Phi_j^*$
$\Rightarrow$ Do this have a physical sens outside of the exchange energy ?

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Cross charge distribution

We define the **total charge density** n of 2 electrons by :

$$n = \|\Psi_1 \boldsymbol{\chi_1} + \Psi_2 \boldsymbol{\chi_2}\|^2 = |\Psi_1|^2 + |\Psi_2|^2 + (\Psi_1^* \Psi_2 \boldsymbol{\chi_1}^\dagger . \boldsymbol{\chi_2} + \text{c.c}) \tag{11}$$

We have only two bounded electrons ($\int n(\boldsymbol{r}, t) d^3 r = 2$) and because :

$$\int d^3 r (|\Psi_1|^2 + |\Psi_2|^2) = 2 \tag{12}$$

the **cross charge terms** ($\sim$ electron "interference") should vanish :

$$\Rightarrow \int d^3 r (\Psi_1^* \Psi_2 \delta_{s_1, s_2} + \text{c.c}) = 0 \tag{13}$$

$\Rightarrow$ This is the **Pauli exclusion principle in real space** (orthogonality of spins or spatial parts : singlet or triplet state)
Remark : $\Psi_1^* \Psi_2 \delta_{s_1, s_2}$ can be seen as a **source** for **exchange potential**

Transition current

Schrödinger believed : **cross wave functions** quantities → responsible for **light emission** (Schrödinger [3], Boudet [4])
⇒ For a **single** electron in **two states superposition** Ψ_a and Ψ_b we have a transition current :

$$\boldsymbol{j_{b,a}} = \frac{i\hbar q}{m}\left(\Psi_a \nabla \Psi_b^* - \Psi_b^* \nabla \Psi_a\right) = \frac{i\hbar q}{m}\left(\Phi_a \nabla \Phi_b^* - \Phi_b^* \nabla \Phi_a\right) e^{i(E_b - E_a)t/\hbar} \quad (14)$$

Oscillations between states ⇒ act as a ”mini-antenna” in **Maxwell equations** ⇒ electromagnetic field (Boudet [4], Loiselet [5]) :

$$\boldsymbol{A_{b,a}} \simeq i \frac{q\mu_0 \omega_{b,a}}{2\pi r} e^{i(E_b - E_a)(t - r/c)/\hbar} \langle \Phi_b | \boldsymbol{r'} | \Phi_a \rangle \quad (15)$$

⇒ **one photon radiation process**. Computing the Poynting vector $P_{b,a}$:

$$\frac{P_{b,a}}{E_b - E_a} = \frac{q^2 \omega_{b,a}^3 \| \langle \Phi_b | \boldsymbol{r'} | \Phi_a \rangle \|^2}{3\pi \epsilon_0 \hbar c^3} \quad (16)$$

⇒ We obtain the **Einstein spontaneous emission rate** (**without QED**)
⇒ Cross charge densities and transition currents have a **physical sens**

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Relativistic extension : Dirac equation

$\Rightarrow$ We have made a **reminder** on Hartree-Fock approximation
$\Rightarrow$ Enlightened **cross charge distribution** and **transition current**
$\Rightarrow$ But now we need to define a **relativistic 3D+T wave equation**
One electron atom Dirac equation (S.I units, $\mathbf{\Psi}$ 4-spinor) :

$$\widehat{\gamma}_\mu \eta_{\mu,\nu} \left(i\partial_\nu - a_\mu \right) \mathbf{\Psi}(\boldsymbol{r},t) = \frac{mc}{\hbar} \mathbf{\Psi}(\boldsymbol{r},t) \tag{17}$$

with $\widehat{\eta} = (-,+,+,+)$ and $a_\mu = -\delta_{\mu,0} Z/r$ (nucleus attraction)
"Ingredients" we need for two and more electrons :

- electron-electron repulsion 4-potential
- electron-electron 4-exchange

The **electron-electron repulsion** 4-potential is $(v_i, \boldsymbol{a_i})$ given by **Maxwell equations** :

$$\left(\frac{\partial_t^2}{c^2} - \Delta \right) \begin{pmatrix} v_i \\ \boldsymbol{a_i} \end{pmatrix} = 2\pi\alpha \sum_{j \neq i} \begin{pmatrix} \left\| \mathbf{\Psi_j} \right\|^2 \\ (\widehat{\gamma}_0 \mathbf{\Psi_j})^\dagger \widehat{\gamma} \mathbf{\Psi_j} \end{pmatrix} \tag{18}$$

Relativistic extension : 4-exchange

The **electron-electron exchange** 4-potential $(v_{i,j}, \boldsymbol{a_{i,j}})$ defined by **cross charge densities** and **relativistic transition currents** :

$$\left(\frac{\partial_t^2}{c^2} - \Delta\right)\begin{pmatrix} v_{i,j} \\ \boldsymbol{a_{i,j}} \end{pmatrix} = -2\pi\alpha \sum_{j\neq i} \begin{pmatrix} \boldsymbol{\Psi_j}^\dagger \boldsymbol{\Psi_i} \\ \left(\widehat{\gamma}_0 \boldsymbol{\Psi_j}\right)^\dagger \widehat{\boldsymbol{\gamma}} \boldsymbol{\Psi_i} \end{pmatrix} \tag{19}$$

In **stationary states** $(\boldsymbol{\Psi_i} = \boldsymbol{\Phi_i}(\boldsymbol{r}) e^{-iE_i t/\hbar})$ we have the 4-repulsion which is **electrostatic** and **magnetostatic** :

$$\begin{pmatrix} v_i \\ \boldsymbol{a_i} \end{pmatrix} = \frac{\alpha}{2} \sum_{j\neq i} \int d^3 r' \frac{1}{\|\boldsymbol{r} - \boldsymbol{r'}\|} \begin{pmatrix} \left\|\boldsymbol{\Phi_j}(\boldsymbol{r'})\right\|^2 \\ (\widehat{\gamma}_0 \boldsymbol{\Phi_j}(\boldsymbol{r'}))^\dagger \widehat{\boldsymbol{\gamma}} \boldsymbol{\Phi_j}(\boldsymbol{r'}) \end{pmatrix} \tag{20}$$

However the **4-exchange** is time-dependent but above all **retarded** :

$$\begin{pmatrix} v_{i,j} \\ \boldsymbol{a_{i,j}} \end{pmatrix} = -\frac{\alpha}{2} \int d^3 r' \frac{e^{i(E_j - E_i)\left(\|\boldsymbol{r} - \boldsymbol{r'}\| - ct\right)/(\hbar c)}}{\|\boldsymbol{r} - \boldsymbol{r'}\|} \begin{pmatrix} \boldsymbol{\Phi_j}^\dagger(\boldsymbol{r'}) \boldsymbol{\Phi_i}(\boldsymbol{r'}) \\ \left(\widehat{\gamma}_0 \boldsymbol{\Phi_j}(\boldsymbol{r'})\right)^\dagger \widehat{\boldsymbol{\gamma}} \boldsymbol{\Phi_i}(\boldsymbol{r'}) \end{pmatrix} \tag{21}$$

It is a **dynamic interaction** (instead of the dipole approximation of HF)

Proposition : real space Dirac-Hartree-Fock equation

Adding the 4-repulsion and 4-exchange to the Dirac equation, we have for each electron 4-spinor $\boldsymbol{\Psi_i}$ the **real space Dirac-Hartree-Fock equation** :

$$\widehat{\gamma}_\mu \eta_{\mu,\nu} \left[\left(i\partial_\nu - a_{i,\nu} \right) \boldsymbol{\Psi_i} - \sum_{j \neq i} a_{i,j,\nu} \boldsymbol{\Psi_j} \right] = \frac{mc}{\hbar} \boldsymbol{\Psi_i} \tag{22}$$

with $\widehat{\eta} = (-,+,+,+)$, with the associated atomic 4-potential :

$$\Box a_{i,\mu} = 2\pi\alpha \left(\sum_{j \neq i} (\widehat{\gamma}_0 \boldsymbol{\Psi_j})^\dagger \widehat{\gamma}_\mu \boldsymbol{\Psi_j} - 2Z\delta(\boldsymbol{r})\delta_{0,\mu} \right) \tag{23}$$

$$\Box a_{i,j,\mu} = -2\pi\alpha (\widehat{\gamma}_0 \boldsymbol{\Psi_j})^\dagger \widehat{\gamma}_\mu \boldsymbol{\Psi_i} \tag{24}$$

with $\sim$ **exclusion principle** : $\int d^3r \left\| \sum_{i=1}^N \boldsymbol{\Psi_i} \right\|^2 = N \Rightarrow \langle \boldsymbol{\Psi_i} | \boldsymbol{\Psi_j} \rangle = \delta_{i,j}$

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Conclusion and to go further

Arguments for the real space quantum mechanics :

- **Compatible with general relativity** (3D+T Minkowski space)
- **Cross charge density** $\Rightarrow$ **exchange energy** and **exclusion principle**
- **Transition current** $\Rightarrow$ **light emission** (alternative to QED ?)
- Is good enough for **small atoms** (can be approx. as Hartree-Fock)
- Looks like density functional theory but **without arbitrary cross-correlation terms**

Issues, difficulties :

- Real space Dirac-Hartree-Fock equation to be **tested and improved** with the **new relativistic interactions** (magnetostatic repulsion, 4-exchange)
- **Electron correlation**, not reproducible in 3D real space
- Bigger atoms, measurement problem, quantum entanglement, Gaunt and Breit terms in two-body Dirac equation, nucleus 4-potential expression (Lamb Shift ?) ...

References

Thank you for your attention

Contact : oplslt@mail.com

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