

## Theories of quantum mechanics:

Schroedinger (non-relativistic, scalar or 1-component “vector”)

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Klein-Gordon (photons, relativistic)

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Dirac (electrons, relativistic, 4-component vector)

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Quantum electrodynamics (QED, general, excludes gravitational field)

Notes:

**Schroedinger**: non-relativistic, it is good for first 2, maybe 3, rows of the periodic table (that is about  $18/118 = 15\%$  of all the elements). Kohn-Sham is a Schroedinger eq. and the theory has reached its limit of accuracy. In order to reach accuracy in heavier elements as well, one needs to include relativistic effects, which involves other types of eigenvalue problems, that are more general; **Klein-Gordon**: relativistic, accurate for all *integer* spins particles (i.e., bosons, such as photons); **Dirac**: relativist, accurate for all *fractional* spins (such as electrons) accurate for **all** elements of the periodic table; **QED**: Generalization of Dirac in the context of “mean field theory”, e.g., Dynamical mean field theory (DMFT). QED misses only gravitational field, the theory has never failed for all existing particles.

Dirac equation (without Kohn-Sham potential) is

$$H\Psi = \left[ \beta mc^2 + c\boldsymbol{\alpha} \cdot \left( \frac{\hbar}{i} \nabla \right) \right] \Psi = \epsilon\Psi$$

Let's define, using the so-called "correspondence principle" between momentum and operator:

$$\mathbf{p} \equiv \frac{\hbar}{i} \nabla$$

With this definition, Dirac equation becomes:

$$H\Psi = [\beta mc^2 + c\boldsymbol{\alpha} \cdot \mathbf{p}] \Psi = \epsilon\Psi$$

Now the particularity of Dirac formulation is that  $\Psi$  is a 4-component vector, called "spinor":

$$\Psi = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix}$$

Therefore  $\beta$  and  $\alpha$  in Dirac equation are  $4 \times 4$  matrices, defined as:

$$\beta = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \quad \text{and} \quad \alpha = \begin{pmatrix} \mathbf{0} & \boldsymbol{\tau} \\ \boldsymbol{\tau} & \mathbf{0} \end{pmatrix},$$

with  $\mathbf{1}$  and  $\mathbf{0}$  being  $2 \times 2$  identity and null matrices, respectively, and with  $\boldsymbol{\tau}$ , the Pauli matrices...

Pauli matrices are  $\boldsymbol{\tau} = (\boldsymbol{\tau}_x, \boldsymbol{\tau}_y, \boldsymbol{\tau}_z)$ :

$$\begin{aligned}\boldsymbol{\tau}_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \boldsymbol{\tau}_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \boldsymbol{\tau}_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.\end{aligned}$$

This formulation implies that the “scalar product”

$$\boldsymbol{\alpha} \cdot \mathbf{p} \equiv \alpha_x p_x + \alpha_y p_y + \alpha_z p_z$$

is actually a summation of  $4 \times 4$  matrices:

$$\boldsymbol{\alpha} \cdot \mathbf{p} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\tau}_x \\ \boldsymbol{\tau}_x & \mathbf{0} \end{pmatrix} p_x + \begin{pmatrix} \mathbf{0} & \boldsymbol{\tau}_y \\ \boldsymbol{\tau}_y & \mathbf{0} \end{pmatrix} p_y + \begin{pmatrix} \mathbf{0} & \boldsymbol{\tau}_z \\ \boldsymbol{\tau}_z & \mathbf{0} \end{pmatrix} p_z$$

Explicitly, the formulation of the scalar product  $\boldsymbol{\alpha} \cdot \mathbf{p}$  becomes:

$$\left( \begin{array}{cc|cc} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ \hline 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{array} \right) p_x + \left( \begin{array}{cc|cc} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ \hline 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{array} \right) p_y + \left( \begin{array}{cc|cc} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ \hline 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{array} \right) p_z$$

The reason for such construction is to keep valid a series commutation operation (see book of Gordon Baym).

Summing up the 3 matrices gives

$$\boldsymbol{\alpha} \cdot \mathbf{p} = \left( \begin{array}{cc|cc} 0 & 0 & p_z & p_x - ip_y \\ 0 & 0 & p_x + ip_y & -p_z \\ \hline p_z & p_x - ip_y & 0 & 0 \\ p_x + ip_y & -p_z & 0 & 0 \end{array} \right)$$

Adding to it the term  $mc^2\boldsymbol{\beta}$  gives the following Hermitian matrix:

$$H = mc^2\boldsymbol{\beta} + c\boldsymbol{\alpha} \cdot \mathbf{p} = \left( \begin{array}{cc|cc} mc^2 & 0 & cp_z & c(p_x - ip_y) \\ 0 & mc^2 & c(p_x + ip_y) & -cp_z \\ \hline cp_z & c(p_x - ip_y) & -mc^2 & 0 \\ c(p_x + ip_y) & -cp_z & 0 & -mc^2 \end{array} \right)$$

Using back the correspondence definition:

$$\mathbf{p} \equiv \frac{\hbar}{i} \nabla$$

gives the explicit formulation of Dirac hamiltonian:

$$H = \left( \begin{array}{cc|cc} mc^2 & 0 & \frac{\hbar}{i} \partial_z & \frac{c\hbar}{i} \partial_x - i \frac{c\hbar}{i} \partial_y \\ 0 & mc^2 & \frac{c\hbar}{i} \partial_x + i \frac{c\hbar}{i} \partial_y & -\frac{c\hbar}{i} \partial_z \\ \hline \frac{c\hbar}{i} \partial_z & \frac{c\hbar}{i} \partial_x - i \frac{c\hbar}{i} \partial_y & -mc^2 & 0 \\ \frac{c\hbar}{i} \partial_x + i \frac{c\hbar}{i} \partial_y & -\frac{c\hbar}{i} \partial_z & 0 & -mc^2 \end{array} \right)$$

After separating into **real** and **imaginary** parts, one gets  $H =$

$$\left( \begin{array}{cc|cc} mc^2 & 0 & -i\hbar c \frac{\partial}{\partial z} & -\hbar c \frac{\partial}{\partial y} - i\hbar c \frac{\partial}{\partial x} \\ 0 & mc^2 & \hbar c \frac{\partial}{\partial y} - i\hbar c \frac{\partial}{\partial x} & i\hbar c \frac{\partial}{\partial z} \\ \hline -i\hbar c \frac{\partial}{\partial z} & -\hbar c \frac{\partial}{\partial y} - i\hbar c \frac{\partial}{\partial x} & -mc^2 & 0 \\ \hbar c \frac{\partial}{\partial y} - i\hbar c \frac{\partial}{\partial x} & i\hbar c \frac{\partial}{\partial z} & 0 & -mc^2 \end{array} \right)$$

The next 3 things that needs to be addressed are:

- the Kohn-Sham effective potential
- the (current) density
- relativistic exchange-correlations.
- relativistic pseudopotentials

All this is based on the work of Eberhard Engel.

Dirac equation with the Kohn-Sham potential is determined similarly to the “kinetic term”. For this, replace  $mc^2$  by  $V^0$  and  $\mathbf{p}$  by  $\mathbf{V}$ , which gives:

$$\beta V^0 + \boldsymbol{\alpha} \cdot \mathbf{V}^{current}$$

where  $\mathbf{V}^{current} = (V^1, V^2, V^3)$ .

In terms of matrices, it reads as:

$$\left( \begin{array}{cc|cc} V^0 & 0 & V^3 & (V^1 - iV^2) \\ 0 & V^0 & (V^1 + iV^2) & -V^3 \\ \hline V^3 & (V^1 - iV^2) & -V^0 & 0 \\ (V^1 + iV^2) & -V^3 & 0 & -V^0 \end{array} \right)$$

This matrix will need to be added to the “kinetic” part, as shown later.

It is more convenient to merge  $\mathbf{V}^{current}$  with  $V^0$  and form the following 4-components potentials

$$\mathbf{V} = (V^0, V^1, V^2, V^3)$$

Similarly, the density (the same as in standard KS) is replaced by a 4-component vector, called “current-density”:

$$\mathbf{j} \equiv (j^0, j^1, j^2, j^3) = (\rho(r), j_x(r)/c, j_y(r)/c, j_z(r)/c)$$

where

$$j^\mu = \sum_k \Theta_k \psi_k^\dagger \alpha^\mu \psi_k + \text{UV finite correction},$$

- $\Theta_k = 1$  if  $-mc^2 < \epsilon_k \leq \epsilon_F$ ; 0, otherwise
- $\alpha^\mu = \gamma^0 \gamma^\mu$ , the Dirac matrices
- “UV finite correction” is described in details in *Relativistic Electronic Structure Theory*, pages 523-621, Eq. (311), E. Engel (2002).
- Notice that  $j^0$  is the usual density definition in Kohn-Sham, because  $\alpha^0 = \mathbf{1}$ , and  $\Theta$  is the whole eigenvalue spectrum, as  $mc^2 \rightarrow \infty$  (non-relativistic limit).

The Kohn-Sham 4-components potentials,  $\mathbf{V}$ , are defined as in the standard approach, replacing the scalar density  $\rho$  by a vector,  $\mathbf{j}$ :

$$\begin{aligned}\mathbf{V} &= e\mathbf{V}_{ext} + \mathbf{V}_H + \mathbf{V}_{xc} \\ \mathbf{V}_{ext} &= \text{External potential} \\ \mathbf{V}_H &= e^2 \int d\mathbf{s} \frac{\mathbf{j}(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|} \\ V_{xc}^\mu &= \frac{\delta E_{xc}[\mathbf{j}]}{\delta j^\mu(\mathbf{r})}\end{aligned}$$

### Summary of FULL Dirac-Kohn-Sham equations

$$(mc^2 + V^0) \psi_1 + \left( V^3 - ic\hbar \frac{\partial}{\partial z} \right) \psi_3 + \left[ \left( V^1 - c\hbar \frac{\partial}{\partial y} \right) + i \left( -V^2 - c\hbar \frac{\partial}{\partial x} \right) \right] \psi_4 = \epsilon_k \psi_1$$

$$(mc^2 + V^0) \psi_2 + \left[ \left( V^1 + c\hbar \frac{\partial}{\partial y} \right) + i \left( V^2 - c\hbar \frac{\partial}{\partial x} \right) \right] \psi_3 + \left( -V^3 + ic\hbar \frac{\partial}{\partial z} \right) \psi_4 = \epsilon_k \psi_2$$

$$\left( V^3 - ic\hbar \frac{\partial}{\partial z} \right) \psi_1 + \left[ \left( V^1 - c\hbar \frac{\partial}{\partial y} \right) + i \left( -V^2 - c\hbar \frac{\partial}{\partial x} \right) \right] \psi_2 + (-mc^2 - V^3) \psi_3 = \epsilon_k \psi_3$$

$$\left[ \left( V^1 + c\hbar \frac{\partial}{\partial y} \right) + i \left( +V^2 - c\hbar \frac{\partial}{\partial x} \right) \right] \psi_1 + \left( -V^3 + ic\hbar \frac{\partial}{\partial z} \right) \psi_2 + (-mc^2 - V^0) \psi_4 = \epsilon_k \psi_4$$

where

$$V^\mu = \frac{\delta E_{xc}[\mathbf{j}]}{\delta j_\mu(\mathbf{r})} + e^2 \int d\mathbf{s} \frac{j^\mu(\mathbf{s})}{|\mathbf{r} - \mathbf{s}|},$$

$$j^\mu = \sum_k \Theta_k \psi_k^\dagger \alpha^\mu \psi_k + j_{UV}^\mu,$$

with

$$\alpha^\mu = \gamma^0 \gamma^\mu$$

and

$\Theta_k = 1$  if  $-mc^2 < \epsilon_k \leq \epsilon_F$ ; 0, otherwise.

$j_{UV}^\mu$  is defined on page 543 of Relativistic Electronic Structure Theory, E. Engel, and on page 610, Appendix D. Total Energy expression is given on page 545 eq. (66).

The index of the 4-component vectors vary as  $\mu = 0, 1, 2, 3$ .

1) Simplified version with magnetism  $(0, 0, B_z) \rightarrow \mathbf{0}$  and using known non-relativistic spin-density functionals  $E_{xc}(n_\uparrow, n_\downarrow)$  as already implemented in PARSEC (see E. Engel page 552)

$$\left\{ -i\mathbf{c}\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + (\boldsymbol{\beta} - \mathbf{1})mc^2 + \frac{\mathbf{1} + \boldsymbol{\beta}\Sigma_z}{2}\nu_+ + \frac{\mathbf{1} - \boldsymbol{\beta}\Sigma_z}{2}\nu_- \right\} \Psi_k = \epsilon_k \Psi_k$$

where

$$\begin{aligned} \rho_\pm(\mathbf{r}) &= \sum_k \Theta_k \Psi_k^\dagger(\mathbf{r}) \left( \frac{\mathbf{1} \pm \boldsymbol{\beta}\Sigma_z}{2} \right) \Psi_k(\mathbf{r}) \\ \nu_\pm(\mathbf{r}) &= \nu_{ext}(\mathbf{r}) + \nu_H(\mathbf{r}) + \nu_{xc,\pm}(\mathbf{r}) \\ \nu_{xc,\pm}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho_+, \rho_-]}{\delta \rho_\pm(\mathbf{r})} \end{aligned}$$

( $\hbar = 1$ ; relativistic units, see Engel's review, chap 10, for complete definitions) This version is valid only for small  $B_z$ . Notice that  $\Psi_k$  is a spinor, or 4-vector. The  $E_{xc}$  is the LDA or GGA. The term  $(\boldsymbol{\beta} - \mathbf{1})$  subtracts the contribution from the electronic rest mass (see Engel's review, page 550).

2) A version without magnetism reduces to

$$\{-ic\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + (\beta - 1)mc^2 + \nu\} \Psi_k = \epsilon_k \Psi_k$$

where

$$\begin{aligned}\rho(\mathbf{r}) &= \sum_k \Theta_k \Psi_k^\dagger(\mathbf{r}) \Psi_k(\mathbf{r}) \\ \nu(\mathbf{r}) &= \nu_{ext}(\mathbf{r}) + \nu_H(\mathbf{r}) + \nu_{xc}(\mathbf{r}) \\ \nu_{xc}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}\end{aligned}$$

( $\hbar = 1$ ; relativistic units, see Engel's review, chap 10, for complete definitions) Notice that  $\Psi_k$  is a spinor, or 4-vector. The  $E_{xc}$  is the LDA or GGA.

3) Simplified version with general expression for magnetism  $\mathbf{B}$  (with  $\mathbf{B} \rightarrow \mathbf{0}$ ) using published relativistic density functionals for  $E_x(n_\uparrow, n_\downarrow)$ , **not implemented in PARSEC**.

The functionals needed are published here:

M. V. Ramana, A. K. Rajagopal, J. Phys. C **14**, 4291 (1981).

M. V. Ramana, A. K. Rajagopal, J. Phys. C **12**, L845 (1979).

A. H. MacDonald, , J. Phys. C **16**, 3869 (1983).

B. X. Xu, A. K. Rajagopal, and M. V. Ramana, J. Phys. C **17**, 1339 (1984).

Next page shows the formulation. In that case, one cannot separate magnetization and density, using generalized spin-density  $\rho_\pm$  as 2 pages before.

$$\{-ic\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + (\boldsymbol{\beta} - \mathbf{1})mc^2 + \nu - \mu_B\boldsymbol{\beta}\boldsymbol{\Sigma} \cdot \mathbf{B}_s\} \Psi_k = \epsilon_k \Psi_k$$

where

$$\rho(\mathbf{r}) = \sum_k \Theta_k \Psi_k^\dagger(\mathbf{r}) \Psi_k(\mathbf{r})$$

$$m(\mathbf{r}) = -\mu_B \sum_k \Theta_k \Psi_k^\dagger(\mathbf{r}) \boldsymbol{\beta} \Psi_k(\mathbf{r})$$

$$\nu(\mathbf{r}) = \nu_{ext}(\mathbf{r}) + \nu_H(\mathbf{r}) + \frac{\delta E_{xc}[\rho, m]}{\delta \rho(\mathbf{r})} + \frac{\delta E_H^T[\rho, m]}{\delta \rho(\mathbf{r})}$$

$$\mathbf{B}_s(\mathbf{r}) = \mathbf{B}_{ext}(\mathbf{r}) + \frac{\delta E_{xc}[\rho, m]}{\delta m(\mathbf{r})} + \frac{\delta E_H^T[\rho, m]}{\delta m(\mathbf{r})}$$

In practice,  $E_H^T \equiv 0$ , because unknown, and only  $\frac{\delta E_x[\rho, m]}{\delta m(\mathbf{r})}$  is known, not  $\frac{\delta E_c[\rho, m]}{\delta m(\mathbf{r})}$ .

All these formulations satisfy Hohenberg-Kohn theorem (replace Laplacian by Dirac operator). Note that more general formulations are currently being studied using exact-exchange (EXX) and Møller-Plesset (MP2, MP4, etc) correlations, beyond the scope of PARSEC, I guess.

Explicit formulation: Dirac for  $B_Z \rightarrow 0$

$$\begin{aligned}
 (mc^2 + \nu_+(\mathbf{r}))\Psi_1^k - i\hbar c \frac{\partial \Psi_4^k}{\partial x} - \hbar c \frac{\partial \Psi_4^k}{\partial y} - i\hbar c \frac{\partial \Psi_3^k}{\partial z} &= \epsilon_k \Psi_1^k \\
 (mc^2 + \nu_-(\mathbf{r}))\Psi_2^k - i\hbar c \frac{\partial \Psi_3^k}{\partial x} + \hbar c \frac{\partial \Psi_3^k}{\partial y} - i\hbar c \frac{\partial \Psi_4^k}{\partial z} &= \epsilon_k \Psi_2^k \\
 (mc^2 + \nu_-(\mathbf{r}))\Psi_3^k - i\hbar c \frac{\partial \Psi_2^k}{\partial x} - \hbar c \frac{\partial \Psi_2^k}{\partial y} - i\hbar c \frac{\partial \Psi_1^k}{\partial z} &= \epsilon_k \Psi_3^k \\
 (mc^2 + \nu_+(\mathbf{r}))\Psi_4^k - i\hbar c \frac{\partial \Psi_1^k}{\partial x} + \hbar c \frac{\partial \Psi_1^k}{\partial y} - i\hbar c \frac{\partial \Psi_2^k}{\partial z} &= \epsilon_k \Psi_4^k
 \end{aligned}$$

with

$$\begin{aligned}
 \rho_+(\mathbf{r}) &= \sum_k \Theta_k \left( |\Psi_1^k|^2 + |\Psi_4^k|^2 \right) \\
 \rho_-(\mathbf{r}) &= \sum_k \Theta_k \left( |\Psi_2^k|^2 + |\Psi_3^k|^2 \right)
 \end{aligned}$$

and

$$\nu_{\pm} = \nu_{ext}(\mathbf{r}) + \nu_H(\mathbf{r}) + \frac{\delta E_{xc}[\rho_+, \rho_-]}{\delta \rho_{\pm}(\mathbf{r})}$$

Once the SCF is attained, to retrieve the density  $\rho$  and magnetization  $m_z$ , use the following transformation:

$$\rho_{\pm}(\mathbf{r}) \equiv \frac{1}{2} \left[ \rho(\mathbf{r}) \mp \frac{1}{\mu_B} m_z(\mathbf{r}) \right]$$

which is, alternatively,

$$\begin{aligned} \rho(\mathbf{r}) &= \rho_-(\mathbf{r}) + \rho_+(\mathbf{r}) \\ m_z(\mathbf{r}) &= \rho_-(\mathbf{r}) - \rho_+(\mathbf{r}). \end{aligned}$$

The exchange-correlation energy  $E_{xc}[\rho_+, \rho_-]$  is the usual spin-density functionals  $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$ .

$E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$  in the PBE as well as the  $E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}]$  in the LSDA are to be used. They are already parametrized in PARSEC, and most codes, actually.