

9 On Transformed Hamiltonians

9.1 General

If the four-component Dirac equation is approximated by some two-component form, certain savings can be obtained. Typically, the small components are eliminated and two separate equations are introduced for atomic $j = l \pm \frac{1}{2}$ states. For molecules, one typically divides the Hamiltonian into a quasirelativistic (spin-orbit averaged) part and the spin-orbit part, diagonalized at some stage. Special attention must be given to variational stability.

One can follow these developments in Table 2.2 of RTAM I-III and the applications in Table 7.3 of RTAM III. For reviews, see **Hess** and **Marian** (2000a).

9.2 The Foldy-Wouthuysen transformation

Foldy and **Wouthuysen** (1950) presented a systematic procedure for decoupling the large and small components of the Dirac equation,

$$\begin{aligned} h_D &= c\underline{\alpha} \cdot (\underline{p} - e\underline{A}) + \beta mc^2 + e\Phi \\ &= \beta mc^2 + \mathcal{O} + \mathcal{E} \end{aligned} \quad (9.1)$$

(with Φ the Coulomb field) where the "odd", \mathcal{O} , and "even", \mathcal{E} , parts satisfy

$$\begin{aligned} \mathcal{O} &= c\underline{\alpha} \cdot (\underline{p} - e\underline{A}), & \{\beta, \mathcal{O}\} &= 0, \\ \mathcal{E} &= e\Phi, & [\beta, \mathcal{E}] &= 0 \end{aligned} \quad (9.2)$$

Any operator H can be separated to

$$\begin{aligned} \mathcal{O} &= \frac{1}{2}(H - \beta H \beta) \\ \mathcal{E} &= \frac{1}{2}(H + \beta H \beta) \end{aligned} \quad (9.3)$$

We shall annihilate the "odd" part up to some power of $1/mc^2$ through the transformation

$$\Psi' = e^{iS} \Psi \quad (9.4)$$

A good choice is

$$S = \frac{-i\beta\mathcal{O}}{2mc^2} = -i\beta \frac{\underline{\alpha} \cdot \underline{\pi}}{2mc} \quad (9.5)$$

where $\underline{\pi}$ is represents the generalized momentum.

A third order FW Hamiltonian becomes

$$h_D''' = mc^2 e \Psi + \frac{1}{2m} \pi^2 \quad (9.6a)$$

$$- \frac{e}{m} \beta_s \cdot \underline{B} \quad (9.6b)$$

$$- \frac{1}{8m^3 c^2} p^4 \quad (\text{mass-velocity}) \quad (9.6c)$$

$$+ \frac{e}{8m^2 c^2} \nabla \cdot \underline{E} \quad (\text{Darwin}) \quad (9.6d)$$

$$- \frac{e}{2m^3 c^2} \underline{S} \cdot \underline{E} \times \underline{p} \quad (\text{spin-orbit}) \quad (9.6e)$$

$$- \frac{e \hbar}{m} \frac{1}{2m^2 c^2} (\underline{S} \cdot \underline{B}) \pi^2 \quad (\text{rel. corr. to Zeeman}) \quad (9.6f)$$

e is the charge of the particle, $\hbar = 1$, $s = \frac{1}{2}\sigma$. [See **Bjorken-Drell** (1964), eq. (4.5), **Moss** (1973), eq. (9.75)].

This expression can be used in 1st-order perturbation theory like the Pauli one. It is not useful in variational calculations as both the mass-velocity term $h_m = -\frac{1}{8c^2} p^4$ and the Darwin term $h_D = \frac{1}{8c^2} \nabla \underline{E} \cdot \underline{V} - \frac{Ze\pi}{2c^2} \delta(\underline{r})$ are strongly singular. One could just as well use them to first order, $\mathcal{O}(c^{-2})$. Contracted basis sets could however allow variational use.

9.3 The Cowan-Griffin equation

Cowan and **Griffin** (1976) or **Wood** and **Boring** (1978) as well as other authors use the 2nd-order equation of Dirac (1928a), putting all the norm in the large component.

$$\begin{cases} P' + \frac{\kappa}{r} P + (-mc + \frac{V-E}{c}) Q = 0 \\ Q' - \frac{\kappa}{r} Q + (-mc + \frac{E-V}{c}) P = 0 \end{cases} \quad (9.7)$$

$$Q = \frac{c}{mc^2 + E - V} (P' + \frac{\kappa}{r} P) \quad (9.8)$$

$$Q' = \frac{c}{mc^2 + E - V} (P'' + \frac{\kappa}{r} P' - \frac{\kappa}{r^2} P) + \frac{cV'}{(mc^2 + E - V)^2} (P' + \frac{\kappa}{r} P) \quad (9.9)$$

$$\begin{aligned}
& \frac{c}{mc^2 + E - V} \left(P'' + \frac{\kappa}{r} P' - \frac{\kappa}{r^2} P \right) - \frac{\kappa}{r} \frac{c}{mc^2 + E - V} \left(P' + \frac{\kappa}{r} P \right) \\
& \quad + \frac{cV'}{(mc^2 + E - V)^2} \left(P' + \frac{\kappa}{r} P \right) + \frac{-mc^2 + E - V}{c} P = 0 \quad |E = mc^2 + \varepsilon \\
& \quad P'' + \frac{\kappa}{r} P' - \frac{\kappa}{r^2} P - \frac{\kappa}{r} P' - \frac{\kappa^2}{r^2} P + \frac{V'}{2mc^2 + \varepsilon - V} \left(P' + \frac{\kappa}{r} P \right) \\
& \quad \quad \quad + \frac{1}{c^2} (2mc^2 + \varepsilon - V) (\varepsilon - V) P = 0 \\
& \quad P'' - \frac{\kappa(\kappa + 1)}{r^2} P + 2m(\varepsilon - V) P + \underbrace{\frac{V'}{2mc^2 + \varepsilon - V} \left(P' + \frac{\kappa}{r} P \right)}_{h_d + h_{SO}} \\
& \quad \quad \quad + \underbrace{\frac{1}{c^2} (\varepsilon - V)^2}_{h_m} = 0 \tag{9.10}
\end{aligned}$$

$$\kappa(\kappa + 1) = l(l + 1) \tag{9.11}$$

Quasirelativistic usage: put $\int_0^\infty P^2 dr = 1!$ (This is the only approximation!)

Dirac (1928) [PRSL A 117 (1928) 610]: Exact 2nd-order equation.

For the **non-relativistic** case,

$$r \rightarrow 0: \quad P'' = \frac{l(l+1)}{r^2} P \quad \Rightarrow P \propto r^{l+1}, \quad R \propto \frac{P}{r} = r^l \tag{9.12}$$

$$r \rightarrow \infty: \quad P'' = -2m\varepsilon P \quad \Rightarrow P \propto e^{\xi r}, \quad \xi = \sqrt{-2m\varepsilon} \tag{9.13}$$

For the **relativistic** case,

$$p \propto r^\gamma, \quad \gamma = \sqrt{\kappa^2 - \left(\frac{Z}{c}\right)^2} \tag{9.14}$$

9.4 Douglas-Kroll-Hess

Instead of expanding in powers of $1/c$ one can rather expand in powers of the coupling strength, $Z\alpha c\hbar$ (**Douglas** and **Kroll** 1974, **Hess** 1986, **Jansen** and **Hess** 1989). This leads to operators which are bound from below and can be used variationally.

The DK formalism, which is an *all electron* method, is based on a series of unitary transformations U_0, U_1, \dots of which the lowest is the *free-particle FW-transformation* defined by

$$\begin{cases} U_0 = A(1 + \beta R) \\ U_0^{-1} = (R\beta + 1)A \end{cases} \tag{9.15}$$

where we have

$$A = \sqrt{\frac{E_p + mc^2}{2E_p}} \quad (9.16)$$

$$R = \frac{c\underline{\alpha} \cdot \underline{p}}{E_p + mc^2} \quad (9.17)$$

$$E_p = c\sqrt{p^2 + m^2c^2} \quad (9.18)$$

Applying U_0 to $h_D = c\underline{\alpha} \cdot \underline{p} + (\beta - 1)mc^2 + V$ gives

$$U_0 h_D U_0^{-1} = \beta E_p + \mathcal{E}_1 + \mathcal{O}_1 \equiv H_1 \quad (9.19)$$

with

$$\begin{aligned} \mathcal{E}_1 &= A(V + RVR)A \\ \mathcal{O}_1 &= \beta A(RV - VR)A \end{aligned} \quad (9.20)$$

For chemical purposes one more transformation is needed. One uses

$$U_1 = \sqrt{1 + W_1^2} + W_1 \quad (9.21)$$

with W_1 anti-hermitian, $W_1^\dagger = -W_1$. Performing the transformation through U_1 and expanding the square root in powers of W_1 ,

$$\begin{aligned} U_1 H_1 U_1^{-1} &= \beta E_p - [\beta E_p, W_1] + \mathcal{E}_1 + \mathcal{O}_1 \\ &\quad + \frac{1}{2}\beta E_p W_1^2 + \frac{1}{2}W_1^2 \beta E_p - W_1 \beta E_p W_1 \\ &\quad + [W_1, \mathcal{O}_1] + [W_1, \mathcal{E}_1] + \dots \end{aligned} \quad (9.22)$$

omitting higher order terms. The first-order odd term is eliminated by setting

$$[\beta E_p, W_1] = \mathcal{O}_1 \quad (9.23)$$

and solving for W_1 . It's momentum space integral operator is

$$W_1 \Phi(\underline{p}) = \int d^3 p' W_1(\underline{p}, \underline{p}') \Phi(\underline{p}') \quad (9.24)$$

with a kernel

$$W_1(\underline{p}, \underline{p}') = A(R - R') A' \frac{V(\underline{p}, \underline{p}')}{E_{p'} + E_p} \quad (9.25)$$

$V(\underline{p}, \underline{p}')$ is the Fourier transform of the external potential. The primed quantities are expressed in terms of the variable \underline{p}' . The final result is

$$H^{\text{decoupled}} \cong \beta E_p + \mathcal{E}_1 - \beta [W_1 E_p W_1 + \frac{1}{2} [W_1^2, E_p]]. \quad (9.26)$$

The spin-orbit terms can be separated using

$$(\underline{\sigma} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) = \underline{A} \cdot \underline{B} + i\underline{\sigma} \cdot (\underline{A} \times \underline{B}) \quad (9.27)$$

see Hess *et al.* (1995). The final result becomes

$$\begin{aligned} H_{\text{SO}}^+ &= \sum_i^{\text{el.}} \sum_{\alpha}^{\text{nuc.}} e^2 Z_{\alpha} \frac{A_i}{E_i + m} \underline{\sigma}_i \cdot \left(\frac{\underline{r}_{i\alpha}}{r_{i\alpha}} \times \underline{p}_i \right) \frac{A_i}{E_i + m} \\ &\quad - e^2 \sum_{i \neq j} \frac{A_i A_j}{E_i + m} \left(\frac{\underline{r}_{ij}}{r_{ij}^3} \times \underline{p}_i \right) \cdot (\underline{\sigma}_i + 2\underline{\sigma}_j) \frac{A_i A_j}{E_i + m} \end{aligned} \quad (9.28)$$

A series expansion in powers of c^{-2} becomes

$$\frac{A_i}{E_i + mc^2} = \frac{1}{2mc^2} - \frac{3p_i^2}{16m^3c^4} + \dots \quad (9.29)$$

The DK Hamiltonian has now been implemented in a large number of programs, to mention a few: MAGIC, MOLCAS, PARAGAUSS and those by Hess himself.

For calculating properties, the operator has to be transformed as well, if transformed Hamiltonians are used. This could be quite tedious.

9.5 Zero Order Regular Approximation, ZORA

The previous elimination procedures treated $\frac{E-V}{mc^2}$ as a small parameter. Sufficiently near the nucleus this is not true. Here

$$\omega(\underline{r}) = \left(1 - \frac{V-E}{2mc^2} \right) = \sum_{n=0}^{\infty} \left(\frac{V-E}{2mc^2} \right)^n \quad (9.30)$$

will only converge when $|\frac{V-E}{2mc^2}| < 1$. By rewriting the expression as

$$\omega(\underline{r}) = \frac{2mc^2}{2mc^2 - V} \left(1 + \frac{E}{2mc^2 - V} \right)^{-1} \quad (9.31)$$

we obtain an expression in

$$\frac{1}{2mc^2 - V}$$

which will converge. This leads to the Zero (or higher) Order Regular Approximation, **ZORA** (**E. van Lenthe** *et al.* 1993–).

The ZORA-level approximation was already given by **Chang, Péliissier** and **Durand** (1986) or by **Heully** *et al.* (1986).

One problem with ZORA is the electric gauge invariance but this can be approximately remedied (**E. van Lenthe, Baerends, Snijders** 1994, **van Wüllen** 1998).

The scalar scaled ZORA equation is (**Faas et al.** 2000)

$$\frac{1}{S}[\underline{p} \cdot B \underline{p} + V_c - K_{\Psi\Psi}] \psi_i = \mathcal{E}_i^{\text{scaled}} \psi_i \quad (9.32)$$

with the scaling factor

$$S = 1 + \langle \Psi_i | \underline{p} \cdot \frac{1}{c^2} B^2 \underline{p} | \Psi_i \rangle \quad (9.33)$$

$$B = \frac{c^2}{2c^2 - V_c} \quad (9.34)$$

$$V_c = V_{\text{nuc}} + J_{\psi\psi}$$

J and K are the usual Coulomb and exchange operators, respectively. Van Wüllen's idea was to set $B = B_0 = c^2/(2c^2 - V_0)$, V_0 depending on the atoms only.

ZORA has been implemented in packages as GAMESS-UK, ADF and DIRAC.

F. Wang et al. (2000) include spin-orbit effects at DFT level in

$$[\underline{\sigma} \cdot \underline{p} \frac{c^2}{2c^2 - V_0} \underline{\sigma} \cdot \underline{p} + V] \phi = \mathcal{E} \phi \quad (9.35)$$

The separated SO operator becomes

$$h_{\text{SO}} = i \underline{\sigma} \cdot [\underline{p} \times \frac{V_0}{2(2c^2 - V_0)} \underline{p}] \quad (9.36)$$

9.6 Direct Perturbation Theory, DPT

The wave function and its metric will have to be an analytic function at the limit $c^{-1} \rightarrow 0$.

The Direct Perturbation Theory (DPT) has been developed by **Sewell** (1949), **Titchmarsh** (1962), **Rutkowski** (1986–), **Kutzelnigg** (1989–). See also **Franke** (1994).

Instead of the original Dirac equation

$$\begin{pmatrix} V - E & c \underline{\sigma} \cdot \underline{p} \\ c \underline{\sigma} \cdot \underline{p} & -2mc^2 + V - E \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = 0 \quad (9.37)$$

one now writes

$$\begin{pmatrix} V - E & \underline{\sigma} \cdot \underline{p} \\ \underline{\sigma} \cdot \underline{p} & -2m + t(V - E)/c^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ c\psi_- \end{pmatrix} = 0 \quad (9.38)$$

with the parameter $t = 0$ and $t = 1$ corresponding to the non-relativistic and relativistic cases respectively. The NR case corresponds to the Lévy-Leblond (1967) equation. Both E and

$$\Psi = \begin{pmatrix} \psi_+ \\ c\psi_- \end{pmatrix}$$

are expanded in powers of t (or c^{-2}). A key paper on the subject is Kutzelnigg (1996).

9.7 Further examples

9.7.1 RESC

Hirao (see **Nakajima** *et al.* 1999, 2000) start from the inconvenience of having the energy in the 2nd-order equation

$$\left[V + (\underline{\sigma} \cdot \underline{p}) \frac{c^2}{2mc^2 - V + E} (\underline{\sigma} \cdot \underline{p}) \right] \psi_L = E \psi_L \quad (9.39)$$

$$\langle \psi_L | 1 + x^\dagger x | \psi_L \rangle = 1, \quad \psi_S = X \psi_L$$

They suggest replacing

$$E - V \rightarrow T = \sqrt{m^2 c^4 + p^2 c^2} - mc^2 \quad (9.40)$$

which is independent of the eigenvalue E . The Hamiltonian can again be separated into spin-free and spin-dependent parts.

Barysz (2000) has analyzed this family of **RESC** (Relativistic scheme for Eliminating Small Components) Hamiltonians. Although they can show signs of variational collapse already at moderate Z (≈ 80), the result for valence electrons can be close to Douglas-Kroll ones.

9.7.2 AMFI

The Atomic-Mean-Field-Integral method eliminates the spin-other-orbit terms in terms of an effective one-electron, one-centre potentials. (Hess *et al.* 1996, Marian and **Wahlgren** 1996, Schimmelpfennig *et al.* 1998ab, **Tatchen** and Marian 1999).

An average over the two-electron terms is taken for the valence shell, and thus large two-electron integral files can be avoided.