

6 Molecular Orbital Methods

6.1 Semiempirical methods

As a general philosophy, the purpose of semiempirical calculations is to produce good insight, not to produce bad numbers.

6.1.1 Extended Hückel Methods

Include all valence electrons. Diagonalize an effective, one-electron Hamiltonian

$$[\mathbf{H} - E_i \mathbf{S}] \mathbf{c}_i = 0 \quad (6.1)$$

$$h_{ab} = (KS_{ab}/2)[h_{aa} + h_{bb}] \quad (6.2)$$

$$h_{aa} = \alpha_a \quad (6.3)$$

K is the **Wolfsberg-Helmholz** constant and has a value of 1.75.

The overlap matrix \mathbf{S} is evaluated using (single- or multiple- ζ) Slater orbitals:

$$S_{ab} = \langle a|b \rangle \quad (6.4)$$

The total energy is approximated by the eigenvalue sum

$$E_T = \sum_{i=1}^{\text{occ}} E_i \quad (6.5)$$

Carry out **Mulliken** population analysis. Can be made charge-iterative.

Historical origins:

- Mulliken 1949, Wolfsberg and Helmholz 1952; Eq. (6.2)
- **Longuet-Higgins** *et al.* 1954, **Lipscomb** *et al.* 1961
- **Hoffmann 1963**

Use in "quasirelativistic mode":

- Hoffmann school, including band structures.

For a review on relativistic semiempirical methods, see Pyykkö (1988b).

6.1.2 Zero Differential Overlap Approximation

Include all valence electrons. Start from the Hartree-Fock equations

$$\begin{aligned}\mathbf{F}\psi_1 &= [T + V_n + V_c + V_x]\psi_i \\ &= E_i\psi_i + \sum_{j \neq i} E_{ij}\psi_j\end{aligned}\quad (6.6)$$

and set systematically all products of two AOs,

$$\phi_A\phi_b = \delta_{ab}\phi_a^2 \quad (6.7)$$

in the potentials V_c and V_x , and in \mathbf{S} .

The total energy is calculated as

$$E_T = \langle \Psi | F | \Psi \rangle \quad (6.8)$$

with the single-determinant wave function

$$\Psi = |\psi_1(1)\overline{\psi_1}(2)\dots| \quad (6.9)$$

Various versions

- CNDO (Complete Neglect of Differential Overlap): Include only the integrals

$$\begin{aligned}\langle a_A(1)b_B(1)|r_{12}^{-1}|c_C(2)d_D(2)\rangle \\ = \delta_{AB}\delta_{ab}\delta_{CD}\delta_{cd}(aa|cc)\end{aligned}\quad (6.10)$$

- INDO (Intermediate NDO): Add all one-center integrals. Exchange introduced.

Quasirelativistic ZDO models

- **Boča** 1987–, **Rösch/Zerner** *et al.* 1987–. Use relativistic data.
- **M. J. S. Dewar** *et al.* (1985): Empirical MNDO or AM1 parameters for Hg, Pb. See review by J. J. P. Stewart, *J. Computer-Aided Mol. Design* **4** (1990) 1-105.
- See Table 7.7 of RTAM III (2000).
- **Thiel** and **Voityuk** (1996): MNDO for d-orbitals, Cl–I, Zn–Hg.

6.1.3 Inclusion of Spin-Orbit Splitting

Many calculations since late 1960'ies, see refs. 69-102 in P. Pyykkö, *Methods in Comp. Chem.* **2** (1988) 137-226. Simplest alternative: include the one-center SO term,

$$h_{\text{SO}} = \sum_g^{\text{centers}} \zeta_g \mathbf{l} \cdot \mathbf{s} \quad (6.11)$$

This obviously doubles the Hamiltonian matrix (for α and β spin).

ZDO Methods with SO Splitting

- Boča (1989, 1990ab): Relativistic CNDO/1. Applications on di- and triatomics, Au_6^{2+}, \dots
- Böhm *et al.* (1989): Relativistic ZDO. $\text{Fe}_n, n = 12 - 14$.
- Kotzian *et al.* (1989, 1991, 1992), Kotzian and Rösch (1991, 1992): Relativistic INDO/S – CI ('S' for spectroscopic). Diatomic hydrides and oxides. LnO . $[\text{Ce}(\text{H}_2\text{O})_6]^{3+}$.
- Jahns *et al.* (1992): INDO/1 ('1' for ground state) $[(\text{Cp}_2^*\text{M})_2\text{C}_6\text{H}_4]$, $\text{M} = \text{Sc}, \text{Lu}$. *Agostic* M...H attraction reproduced.
- Minaev *et al.* (1989): Relativistic MINDO/3 – CI. Diatomic hydride systems. Intensity borrowing.
- Roszak and Lipiński (1992): INDO. Triplet – singlet lifetimes of pyridine etc.

6.1.4 Relativistic Extended Hückel (REX)

- Introduce $|lsjm\rangle$ basis with separate energy parameters, α_a and radial parameters ζ_a for the SO-split atomic states.
- Derive these parameters from *ab initio* atomic calculations, thus extrapolating them to the molecular domain (Lohr and Pyykkö 1979). R/NR!
- Rösch (1983) treated the *Kramers degeneracy* algebraically (QATREX)
- Larsson and Pyykkö (1986): Charge iterations added (ITEREX)
- Original default parameters (in 'DEFPAR') acceptable for main-group elements. Realistic parameters for the actinides in Pyykkö, Laakkonen and Tatsumi, *Inorg. Chem.* (28) (1989) 1801.
- Always carry out a *sensitivity study* with respect to parameters or try to confirm the ideas found by better methods.

Some Results by REX

- Implement the relativistic theory of nuclear spin-spin coupling constants. New terms. See Pyykkö and **Wiesenfeld** (1981).
- Symmetry rules for the spin-spin coupling tensor, **J, A. D. Buckingham** *et al.* (1982).
- Transparent interpretation of the *heavy-atom chemical shift* in ^1HX NMR, Pyykkö, **Görling** and Rösch (1987). "HAHA" (1987).
- The *6p-hole theory* of actinyl NQCC, Larsson and Pyykkö (1986).
- Colors of BiPh_5 and PbCl_6^{2-} attributed to the relativistic stabilization of the $6s_{a_1}$ LUMO (**Schmuck** *et al.* (1990), **El-Issa** *et al.* (1991)).
- The SO splitting of the OsO_4 valence $3t_2$ MO attributed to $5p$ semicore character, in most models. Pyykkö, **Li, Bastug, Fricke** and **Kolb** (1993).

6.2 One-Electron Molecules

6.2.1 The Hamiltonian

$$h = T + V, \quad V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \quad (6.12)$$

6.2.2 Possible Coordinate Systems

a) Elliptical:

$$\begin{cases} \xi = (r_1 + r_2)/R, & 1 \leq \xi < \infty \\ \eta = (r_1 - r_2)/R, & -1 \leq \eta \leq 1 \end{cases} \quad (6.13)$$

$$\begin{cases} r_1 = \frac{R}{2}(\xi + \eta) \\ r_2 = \frac{R}{2}(\xi - \eta) \end{cases} \quad (6.14)$$

Constant ξ : ellipses, constant η : hyperbolas.

Third variable: ϕ .

$$dV = \frac{R^3}{8}(\xi^2 - \eta^2)d\xi d\eta d\phi \quad (6.14')$$

Then

$$h\psi = E\psi \quad (6.15)$$

$$\psi = e^{im\phi} f(\xi, \eta) \quad (6.16)$$

$$V(\xi, \eta) = -\frac{2Z_1}{R(\xi + \eta)} - \frac{2Z_2}{R(\xi - \eta)} \quad (6.17)$$

The Schrödinger equation:

$$\left[-\frac{2}{R^2(\xi^2 - \eta^2)} \left(\frac{\partial}{\partial \xi}(\xi^2 - 1) \frac{\partial}{\partial \xi} + \frac{\partial}{\partial \eta}(1 - \eta^2) \frac{\partial}{\partial \eta} - m^2 \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right) \right) + V(\xi, \eta) - E \right] f(\xi, \eta) = 0 \quad (6.18)$$

Ø. Burrau, *Mat. fys. Medd.* **7** (1927)

D. R. Bates, K. Ledsham, A. L. Stewart, *Phil. Trans. RSL* **246** (1953) 215.

See L. Laaksonen *et al.* (1983a).

Eq. (6.18) separates,

$$f(\xi, \eta) = L(\xi)M(\eta) \quad (6.19)$$

The eigenvalues E are obtained from the truncation of the series for $L(\xi)$.

b) The variable q :

$$\eta = 1 - N \ln q, \quad 0 \leq q \leq 1 \quad (6.20)$$

c) The variable t :

$$t = \ln \xi \quad (6.21)$$

d) Prolate spheroidal:

The 2D-program uses the variables (μ, ν) :

$$\begin{cases} \xi = \cosh \mu, & 0 \leq \mu < \infty \\ \eta = \cos \nu, & 0 \leq \nu \leq \pi \end{cases} \quad (6.22)$$

$$\begin{cases} r_1 = \frac{1}{2}R(\cosh \mu + \cos \nu) \\ r_2 = \frac{1}{2}R(\cosh \mu - \cos \nu) \end{cases} \quad (6.23)$$

$$dV = \frac{R^3}{8} \sinh \mu \sin \nu (\cosh^2 \mu - \cos^2 \nu) d\mu d\nu d\phi \quad (6.24)$$

$$\psi = e^{im\phi} f(\mu, \nu) \quad (6.25)$$

$$\begin{aligned} \frac{\nabla^2 \psi}{e^{im\phi}} &= \frac{4}{R^2 (\cosh^2 \mu - \cos^2 \nu)} \left[\frac{\partial^2}{\partial \mu^2} + \coth \mu \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} \right. \\ &\quad \left. + \cot \nu \frac{\partial}{\partial \nu} - m^2 \left(\frac{1}{\sinh^2 \mu} + \frac{1}{\sin^2 \nu} \right) \right] f(\mu, \nu) \end{aligned} \quad (6.26)$$

e) Kolb's coordinates (s, t) :

See C. Düsterhöft, L. Yang, D. Heinemann, D. Kolb, *Chem. Phys. Lett.* **229** (1994) 667.

$$\begin{aligned} \eta &= 4 \sinh^4 s + 1, & 0 \leq s < \infty \\ \xi &= \cos t \left[1 + \frac{1}{2} \sin^2 t \right], & 0 \leq t \leq \pi \end{aligned} \quad (6.27)$$

[Already in L. Yang *et al.*, *Chem. Phys. Lett.* **178** (1991) 213]

6.2.3 Transformation of the Dirac Equation

D. Sundholm, P. Pyykkö, L. Laaksonen, *Phys. Scripta* **36** (1987) 400.
D. Sundholm, *Chem. Phys. Lett.* **223** (1994) 469.

Consider the Dirac hamiltonian

$$h_D = \begin{pmatrix} V & c\underline{\sigma} \cdot \underline{p} \\ c\underline{\sigma} \cdot \underline{p} & V - 2c^2 \end{pmatrix} \quad (6.28)$$

$$\underline{\sigma} \cdot \underline{p} = \begin{pmatrix} p_z & p_x - ip_y \\ p_x + ip_y & -p_z \end{pmatrix} \quad (6.29)$$

Let

$$\Psi = \begin{pmatrix} \psi_L \\ \psi_S \end{pmatrix} = \begin{pmatrix} e^{i(m-\frac{1}{2})\phi} \psi_1^L(\mu, \nu) \\ e^{i(m+\frac{1}{2})\phi} \psi_2^L(\mu, \nu) \\ ie^{i(m-\frac{1}{2})\phi} \psi_1^S(\mu, \nu) \\ ie^{i(m+\frac{1}{2})\phi} \psi_2^S(\mu, \nu) \end{pmatrix} \quad (6.30)$$

The lower equation from (6.28) gives

$$\begin{aligned} c\underline{\sigma} \cdot \underline{p} \psi_L + (V - 2c^2) \psi_S &= E \psi_S \Rightarrow \\ \psi_S &= \frac{c\underline{\sigma} \cdot \underline{p}}{2c^2 + E - V} \psi_L \end{aligned} \quad (6.31)$$

This can be substituted in the upper equation,

$$\begin{aligned}(V - E)\psi_L &= -c\underline{\sigma} \cdot \underline{p}\psi_S \\ &= -c\underline{\sigma} \cdot \underline{p}(2c^2 + E - V)^{-1}c\underline{\sigma} \cdot \underline{p}\psi_L\end{aligned}\quad (6.32)$$

Letting

$$f(\underline{r}) = \frac{c^2}{2c^2 + E - V}, \quad (6.33)$$

$$\begin{aligned}[\underline{\sigma} \cdot \underline{p}f(\underline{r})\underline{\sigma} \cdot \underline{p} + V - E]\psi_L &= 0 \\ \underline{p} &= -i\nabla, \quad p^2 = -\nabla^2, \quad ip = \nabla\end{aligned}\quad (6.34)$$

Recalling

$$(\underline{\sigma} \cdot \underline{A})(\underline{\sigma} \cdot \underline{B}) = \underline{A} \cdot \underline{B} + i\underline{\sigma} \cdot (\underline{A} \times \underline{B}) \quad [3.88]$$

$$\begin{aligned}\underline{\sigma} \cdot \underline{p}f(\underline{r})\underline{\sigma} \cdot \underline{p} &= \underline{\sigma} \cdot \left[\underbrace{(\underline{p}f)}_{\underline{A}} \cdot \underbrace{\underline{\sigma} \cdot \underline{p}}_{\underline{B}} + f\underline{p}(\underline{\sigma} \cdot \underline{p}) \right] \\ &= (\underline{p}f) \cdot \underline{p} + i\underline{\sigma} \cdot (\underline{p}f \times \underline{p}) + f \left[\underbrace{(\underline{\sigma} \cdot \underline{p})(\underline{\sigma} \cdot \underline{p})}_{p^2 + i\underline{\sigma} \cdot (\underline{p} \times \underline{p})} \right] \\ &= fp^2 + (\underline{p}f) \cdot \underline{p} + i\underline{\sigma} \cdot (\underline{p}f \times \underline{p}) \\ &= -f\nabla^2 - \nabla f \cdot \nabla - i\underline{\sigma} \cdot (\nabla f \times \nabla)\end{aligned}\quad (6.35)$$

In an orthogonal coordinate system,

$$\nabla f = \hat{e}_1 \frac{1}{h_1} \frac{\partial f}{\partial q_1} + \hat{e}_2 \frac{1}{h_2} \frac{\partial f}{\partial q_2} + \hat{e}_3 \frac{1}{h_3} \frac{\partial f}{\partial q_3} \quad (6.36)$$

(The distance, $ds_i = h_i dq_i$). Here

$$\begin{aligned}h_\mu = h_\nu &= \frac{R}{2} \sqrt{(\cosh^2 \mu - \cos^2 \nu)} \\ h_\phi &= \frac{R}{2} \sinh \mu \sin \nu\end{aligned}\quad (6.37)$$

where all the h s are weight functions.

Then

$$\begin{aligned}-\nabla f \cdot \nabla \psi &= -\frac{1}{h_\mu^2} \frac{\partial f}{\partial \mu} \frac{\partial \psi}{\partial \mu} - \frac{1}{h_\nu^2} \frac{\partial f}{\partial \nu} \frac{\partial \psi}{\partial \nu} - \frac{1}{h_\phi^2} \frac{\partial f}{\partial \phi} \frac{\partial \psi}{\partial \phi} \\ &= -\frac{4}{R^2(\cosh^2 \mu - \cos^2 \nu)} \left[\frac{\partial f}{\partial \mu} \frac{\partial \psi}{\partial \mu} + \frac{\partial f}{\partial \nu} \frac{\partial \psi}{\partial \nu} \right] \\ &\quad - \frac{4}{R^2 \sinh^2 \mu \sin^2 \nu} \frac{\partial f}{\partial \phi} \frac{\partial \psi}{\partial \phi}\end{aligned}\quad (6.38)$$

$$\begin{aligned}
-f\nabla^2 = & -\frac{4f}{R^2(\cosh^2\mu - \cos^2\nu)} \left[\frac{\partial^2}{\partial\mu^2} + \frac{\cosh\mu}{\sinh\mu} \frac{\partial}{\partial\mu} \right. \\
& \left. + \frac{\partial^2}{\partial\nu^2} + \frac{\cos\nu}{\sin\nu} \frac{\partial}{\partial\nu} + \frac{\cosh^2\mu - \cos^2\nu}{\sinh^2\mu \sin^2\nu} \frac{\partial^2}{\partial\phi^2} \right] \quad (6.39)
\end{aligned}$$

What, then, is $-\underline{i}\sigma \cdot \underbrace{(\nabla f \times \nabla\psi)}_{\underline{D}}$?

On one hand,

$$\nabla f \times \nabla\psi = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} & \frac{\partial f}{\partial z} \\ \frac{\partial \psi}{\partial x} & \frac{\partial \psi}{\partial y} & \frac{\partial \psi}{\partial z} \end{vmatrix} \quad (6.40)$$

(all h s equal 1 in cartesian coordinates)

On the other hand, denoting $f_x \equiv \frac{\partial f}{\partial x}$,

$$\begin{aligned}
\nabla f \times \nabla\psi &= \begin{vmatrix} \hat{e}_\mu & \hat{e}_\nu & \hat{e}_\phi \\ \frac{1}{h_\mu} f_\mu & \frac{1}{h_\nu} f_\nu & \frac{1}{h_\phi} f_\phi \\ \frac{1}{h_\mu} \psi_\mu & \frac{1}{h_\nu} \psi_\nu & \frac{1}{h_\phi} \psi_\phi \end{vmatrix} \\
&= \hat{e}_\mu \frac{1}{h_\nu h_\phi} (f_\nu \psi_\phi - f_\phi \psi_\nu) + \hat{e}_\nu \frac{1}{h_\phi h_\mu} (f_\phi \psi_\mu - f_\mu \psi_\phi) \\
&\quad + \hat{e}_\phi \frac{1}{h_\mu h_\nu} (f_\mu \psi_\nu - f_\nu \psi_\mu)
\end{aligned} \quad (6.41)$$

We will need the cartesian components of this determinant,

$$\underline{D} = D_1 \hat{e}_1 + D_2 \hat{e}_2 + D_3 \hat{e}_3 \quad (6.42)$$

for the scalar product with

$$\underline{\sigma} = \sigma_1 \hat{e}_1 + \sigma_2 \hat{e}_2 + \sigma_3 \hat{e}_3 \quad (6.43)$$

$$\begin{cases} \sigma_\mu = \frac{1}{h_\mu} (\sigma_x \frac{\partial x}{\partial \mu} + \sigma_y \frac{\partial y}{\partial \mu} + \sigma_z \frac{\partial z}{\partial \mu}) \\ \sigma_\nu = \frac{1}{h_\nu} (\sigma_x \frac{\partial x}{\partial \nu} + \sigma_y \frac{\partial y}{\partial \nu} + \sigma_z \frac{\partial z}{\partial \nu}) \\ \sigma_\phi = \frac{1}{h_\phi} (\sigma_x \frac{\partial x}{\partial \phi} + \sigma_y \frac{\partial y}{\partial \phi} + \sigma_z \frac{\partial z}{\partial \phi}) \end{cases} \quad (6.44)$$

$$\begin{aligned}
& -i\sigma \cdot (\nabla f \times \nabla \psi) = \\
& -\frac{i}{h_\mu h_\nu h_\phi} \left[(\sigma_x \frac{\partial x}{\partial \mu} + \sigma_y \frac{\partial y}{\partial \mu} + \sigma_z \frac{\partial z}{\partial \mu})(f_\nu \psi_\phi - f_\phi \psi_\nu) \right. \\
& \quad + (\sigma_x \frac{\partial x}{\partial \nu} + \sigma_y \frac{\partial y}{\partial \nu} + \sigma_z \frac{\partial z}{\partial \nu})(f_\phi \psi_\mu - f_\mu \psi_\phi) \\
& \quad \left. + (\sigma_x \frac{\partial x}{\partial \phi} + \sigma_y \frac{\partial y}{\partial \phi} + \sigma_z \frac{\partial z}{\partial \phi})(f_\mu \psi_\nu - f_\nu \psi_\mu) \right] \quad (6.45)
\end{aligned}$$

From

$$\begin{cases} x = \frac{R}{2} \sinh \mu \sin \nu \cos \phi \\ y = \frac{R}{2} \sinh \mu \sin \nu \sin \phi \\ z = \frac{R}{2} \cosh \mu \cos \nu \quad (z \text{ is in the molecular axis direction}) \end{cases} \quad (6.46)$$

$$\begin{cases} \frac{\partial x}{\partial \mu} = \frac{R}{2} \cosh \mu \sin \nu \cos \phi, & \frac{\partial x}{\partial \nu} = \frac{R}{2} \sinh \mu \cos \nu \cos \phi, \\ & \frac{\partial x}{\partial \phi} = \frac{R}{2} \sinh \mu \sin \nu \sin \phi \\ \frac{\partial y}{\partial \mu} = \frac{R}{2} \cosh \mu \sin \nu \sin \phi, & \frac{\partial y}{\partial \nu} = \frac{R}{2} \sinh \mu \cos \nu \sin \phi, \\ & \frac{\partial y}{\partial \phi} = \frac{R}{2} \sinh \mu \sin \nu \cos \phi \\ \frac{\partial z}{\partial \mu} = \frac{R}{2} \sinh \mu \cos \nu, & \frac{\partial z}{\partial \nu} = -\frac{R}{2} \cosh \mu \sin \nu, \\ & \frac{\partial z}{\partial \phi} = 0 \end{cases} \quad (6.47)$$

$$\begin{aligned}
-i\sigma \cdot \underline{D} &= -\frac{iR/2}{h_\mu h_\nu h_\phi} \left[\right. \\
& (\sigma_x \cosh \mu \sin \nu \cos \phi + \sigma_y \cosh \mu \sin \nu \sin \phi + \sigma_z \sinh \mu \cos \nu)(f_\nu \psi_\phi - f_\phi \psi_\nu) \\
& + (\sigma_x \sinh \mu \cos \nu \cos \phi + \sigma_y \sinh \mu \cos \nu \sin \phi - \sigma_z \cosh \mu \sin \nu)(f_\phi \psi_\mu - f_\mu \psi_\phi) \\
& \left. + (-\sigma_x \sinh \mu \sin \nu \sin \phi + \sigma_y \sinh \mu \sin \nu \cos \phi + 0)(f_\mu \psi_\nu - f_\nu \psi_\mu) \right] \quad (6.48)
\end{aligned}$$

$$\left\{ \begin{array}{l} -\sigma_x D_x = -\frac{R}{2} \frac{\sigma_x}{h_\mu h_\nu h_\phi} \left[\cosh \mu \sin \nu \cos \phi (f_\nu \psi_\phi - f_\phi \psi_\nu) \right. \\ \quad \left. + \sinh \mu \cos \nu \cos \phi (f_\phi \psi_\mu - f_\mu \psi_\phi) - \sinh \mu \sin \nu \sin \phi (f_\mu \psi_\nu - f_\nu \psi_\mu) \right] \\ -\sigma_y D_y = -\frac{R}{2} \frac{\sigma_y}{h_\mu h_\nu h_\phi} \left[\cosh \mu \sin \nu \sin \phi (f_\nu \psi_\phi - f_\phi \psi_\nu) \right. \\ \quad \left. + \sinh \mu \cos \nu \sin \phi (f_\phi \psi_\mu - f_\mu \psi_\phi) - \sinh \mu \sin \nu \cos \phi (f_\mu \psi_\nu - f_\nu \psi_\mu) \right] \\ -\sigma_z D_z = -\frac{R}{2} \frac{\sigma_z}{h_\mu h_\nu h_\phi} \left[\sinh \mu \cos \nu (f_\nu \psi_\phi - f_\phi \psi_\nu) \right. \\ \quad \left. - \cosh \mu \sin \nu (f_\phi \psi_\mu - f_\mu \psi_\phi) \right] \end{array} \right. \quad (6.49)$$

Recall that

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$-i\vec{\sigma} \cdot \underline{D} = -\frac{iR/2}{h_\mu h_\nu h_\phi} \times \left(\begin{array}{l} \cosh \mu \sin \nu \cos \phi (f_\nu \psi_\phi - f_\phi \psi_\nu) \\ + \sinh \mu \cos \nu \cos \phi (f_\phi \psi_\mu - f_\mu \psi_\phi) \\ - \sinh \mu \sin \nu \sin \phi (f_\mu \psi_\nu - f_\nu \psi_\mu) \\ \sinh \mu \cos \nu (f_\nu \psi_\phi - f_\phi \psi_\nu) \\ - \cosh \mu \sin \nu (f_\phi \psi_\mu - f_\mu \psi_\phi) \\ -i \left[\cosh \mu \sin \nu \sin \phi (f_\nu \psi_\phi - f_\phi \psi_\nu) \right. \\ \quad \left. + \sinh \mu \cos \nu \sin \phi (f_\phi \psi_\mu - f_\mu \psi_\phi) \right. \\ \quad \left. + \sinh \mu \sin \nu \cos \phi (f_\mu \psi_\nu - f_\nu \psi_\mu) \right] \\ \cosh \mu \sin \nu \cos \phi (f_\nu \psi_\phi - f_\phi \psi_\nu) \\ + \sinh \mu \cos \nu \cos \phi (f_\phi \psi_\mu - f_\mu \psi_\phi) \\ - \sinh \mu \sin \nu \sin \phi (f_\mu \psi_\nu - f_\nu \psi_\mu) \\ +i \left[\cosh \mu \sin \nu \sin \phi (f_\nu \psi_\phi - f_\phi \psi_\nu) \right. \\ \quad \left. + \sinh \mu \cos \nu \sin \phi (f_\phi \psi_\mu - f_\mu \psi_\phi) \right. \\ \quad \left. + \sinh \mu \sin \nu \cos \phi (f_\mu \psi_\nu - f_\nu \psi_\mu) \right] \\ - \sinh \mu \cos \nu (f_\nu \psi_\phi - f_\phi \psi_\nu) \\ + \cosh \mu \sin \nu (f_\phi \psi_\mu - f_\mu \psi_\phi) \end{array} \right)$$

It can be noted that the matrix in the above equation is of the form

$$\begin{pmatrix} a & u - i[v] \\ u + i[v] & -a \end{pmatrix}.$$

$$\begin{aligned}
-i\sigma \cdot \underline{D} = & -\frac{iR/2}{\frac{R^3}{2}(\cosh^2 \mu - \cos^2 \nu) \sinh \mu \sin \nu} \times & (6.50) \\
& \left(\begin{array}{ll}
\sinh \mu \cos \nu (f_\nu \psi_\phi - f_\phi \psi_\nu) & \cosh \mu \sin \nu (\cos \psi - i \sin \phi) (f_\nu \psi_\phi - f_\phi \psi_\nu) \\
-\cosh \mu \sin \nu (f_\phi \psi_\mu - f_\mu \psi_\phi) & + \sinh \mu \cos \nu (\cos \phi - i \sin \phi) (f_\phi \psi_\mu - f_\mu \psi_\phi) \\
\cosh \mu \sin \nu (\cos \psi + i \sin \phi) (f_\nu \psi_\phi - f_\phi \psi_\nu) & - \sinh \mu \sin \nu (\sin \phi + i \cos \phi) (f_\mu \psi_\nu - f_\nu \psi_\mu) \\
+ \sinh \mu \cos \nu (\cos \phi + i \sin \phi) (f_\phi \psi_\mu - f_\mu \psi_\phi) & - \sinh \mu \cos \nu (f_\nu \psi_\phi - f_\phi \psi_\nu) \\
- \sinh \mu \sin \nu (\sin \phi - i \cos \phi) (f_\mu \psi_\nu - f_\nu \psi_\mu) & + \cosh \mu \sin \nu (f_\phi \psi_\mu - f_\mu \psi_\phi)
\end{array} \right)
\end{aligned}$$

Now note that

$$\begin{aligned}
f_\mu = \frac{c^2(-1)}{(2c^2 + E - V)^2} \left(-\frac{\partial V}{\partial \mu}\right), \quad f_\nu = \frac{c^2(-1)}{(2c^2 + E - V)^2} \left(-\frac{\partial V}{\partial \nu}\right), & (6.51) \\
f_\phi \propto \frac{\partial V}{\partial \phi} = 0, &
\end{aligned}$$

$$\cos \phi \mp i \sin \phi = \begin{cases} e^{-i\phi} \\ e^{i\phi} \end{cases}, \quad \sin \phi \pm i \cos \phi = \begin{cases} ie^{-i\phi} \\ -ie^{i\phi} \end{cases} \quad (6.52)$$

$$\begin{aligned}
-I\sigma \cdot \underline{D} = & -\frac{4i}{R^2(\cosh^2 \mu - \cos^2 \nu) \sinh \mu \sin \nu} \times \frac{c^2}{(2c^2 + E - V)^2} \times & (6.53) \\
& \left(\begin{array}{ll}
\sinh \mu \cos \nu \frac{\partial V}{\partial \nu} \psi_\phi & \cosh \mu \sin \nu e^{-i\phi} \frac{\partial V}{\partial \nu} \psi_\phi \\
+\cosh \mu \sin \nu \frac{\partial V}{\partial \mu} \psi_\phi & - \sinh \mu \cos \nu e^{-i\phi} \frac{\partial V}{\partial \mu} \psi_\phi \\
\cosh \mu \sin \nu e^{i\phi} \frac{\partial V}{\partial \nu} \psi_\phi & - \sinh \mu \sin \nu (ie^{-i\phi}) \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu}\right) \psi \\
- \sinh \mu \cos \nu e^{i\phi} \frac{\partial V}{\partial \mu} \psi_\phi & - \sinh \mu \cos \nu \frac{\partial V}{\partial \nu} \psi_\phi \\
+ \sinh \mu \sin \nu (ie^{i\phi}) \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu}\right) \psi & - \cosh \mu \sin \nu \frac{\partial V}{\partial \mu} \psi_\phi
\end{array} \right)
\end{aligned}$$

Recalling the Ansatz (6.30),

$$\begin{aligned}\psi &= \begin{pmatrix} e^{i(m-\frac{1}{2})\phi}\psi_1^L(\mu, \nu) \\ e^{i(m+\frac{1}{2})\phi}\psi_2^L(\mu, \nu) \\ ie^{i(m-\frac{1}{2})\phi}\psi_1^S(\mu, \nu) \\ ie^{i(m+\frac{1}{2})\phi}\psi_2^S(\mu, \nu) \end{pmatrix}, \\ \psi_\phi &= \begin{pmatrix} i(m-\frac{1}{2})e^{i(m-\frac{1}{2})\phi}\psi_1^L(\mu, \nu) \\ i(m+\frac{1}{2})e^{i(m+\frac{1}{2})\phi}\psi_2^L(\mu, \nu) \\ -(m-\frac{1}{2})e^{i(m-\frac{1}{2})\phi}\psi_1^S(\mu, \nu) \\ -(m+\frac{1}{2})e^{i(m+\frac{1}{2})\phi}\psi_2^S(\mu, \nu) \end{pmatrix} = \frac{\partial\psi}{\partial\phi}\end{aligned}\tag{6.54}$$

the operation $-i\sigma \cdot \underline{D}$ gives for the upper row:

$$\begin{aligned}\text{Ai} \left\{ \right. & \left[\sinh \mu \cos \nu \frac{\partial V}{\partial \nu} + \cosh \mu \sin \nu \frac{\partial V}{\partial \mu} \right] i(m-\frac{1}{2})\psi_1^L e^{i(m-\frac{1}{2})\phi} \\ & + \left[\cosh \mu \sin \nu \frac{\partial V}{\partial \nu} - \sinh \mu \cos \nu \frac{\partial V}{\partial \mu} \right] e^{-i\phi} i(m+\frac{1}{2})e^{i(m+\frac{1}{2})\phi}\psi_2^L \\ & \left. - \sinh \mu \sin \nu ie^{-i\phi} e^{i(m+\frac{1}{2})\phi} \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \psi_2^L \right\}\end{aligned}$$

$$A = -\frac{4c^2}{R^2(\cosh^2 \mu - \cos^2 \nu) \sinh \mu \sin \nu (2c^2 + E - V)^2}\tag{6.56}$$

and for the lower row:

$$\begin{aligned}\text{Ai} \left\{ \right. & \left[\cosh \mu \sin \nu \frac{\partial V}{\partial \nu} - \sinh \mu \cos \nu \frac{\partial V}{\partial \mu} \right] e^{i\phi} i(m-\frac{1}{2})e^{i(m-\frac{1}{2})\phi}\psi_1^L \\ & + \sinh \mu \sin \nu ie^{i\phi} e^{i(m-\frac{1}{2})\phi} \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \psi_1^L \\ & \left. - \left[\sinh \mu \cos \nu \frac{\partial V}{\partial \nu} + \cosh \mu \sin \nu \frac{\partial V}{\partial \mu} \right] i(m+\frac{1}{2})e^{i(m+\frac{1}{2})\phi}\psi_2^L \right\}\end{aligned}\tag{6.57}$$

Dividing away the $e^{i\phi}$ -factors

$$\Rightarrow -i\sigma \cdot \underline{D} = \quad (6.58)$$

$$\left(\begin{array}{l} -A \left\{ \left[\sinh \mu \cos \nu \frac{\partial V}{\partial \nu} + \cosh \mu \sin \nu \frac{\partial V}{\partial \mu} \right] (m - \frac{1}{2}) \psi_1^L \right. \\ \quad + \left[\left(\cosh \mu \sin \nu \frac{\partial V}{\partial \nu} - \sinh \mu \cos \nu \frac{\partial V}{\partial \mu} \right) (m + \frac{1}{2}) \right. \\ \quad \quad \left. \left. - \sinh \mu \sin \nu \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \right] \psi_2^L \right\} \\ \\ -A \left\{ \left[\left(\cosh \mu \sin \nu \frac{\partial V}{\partial \nu} - \sinh \mu \cos \nu \frac{\partial V}{\partial \mu} \right) (m - \frac{1}{2}) \right. \right. \\ \quad + \sinh \mu \sin \nu \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \right] \psi_1^L \\ \quad \left. \left. - \left[\sinh \mu \cos \nu \frac{\partial V}{\partial \nu} + \cosh \mu \sin \nu \frac{\partial V}{\partial \mu} \right] (m + \frac{1}{2}) \psi_2^L \right\} \right)$$

Using the definition of A , (6.56),

$$\Rightarrow -i\sigma \cdot \underline{D} = + \frac{4}{R^2(\cosh^2 \mu - \cos^2 \nu)} \frac{f}{2c^2 + E - V} \times \quad (6.59)$$

$$\left(\begin{array}{l} \left[\frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \nu} + \frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \mu} \right] (m - \frac{1}{2}) \psi_1^L \\ \quad + \left[\left(\frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \nu} - \frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \mu} \right) (m + \frac{1}{2}) \right. \\ \quad \quad \left. - \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \right] \psi_2^L \\ \\ \left[\left(\frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \nu} - \frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \mu} \right) (m - \frac{1}{2}) \right. \\ \quad + \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \right] \psi_1^L \\ \quad \left. - \left[\frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \nu} + \frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \mu} \right] (m + \frac{1}{2}) \psi_2^L \right)$$

Combining this result with the *diagonal kinetic energy terms* (6.38)–(6.39) and $(V - E)\psi$, noting that in (6.38)

$$-\nabla f \cdot \nabla \psi = - \frac{4}{R^2(\cosh^2 \mu - \cos^2 \nu)} \frac{f}{2c^2 + E - V} \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \mu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \nu} \right) \psi$$

the upper equation finally becomes

$$\begin{aligned}
& -\frac{4f}{R^2(\cosh^2 \mu - \cos^2 \nu)} \left\{ \left[+\frac{\partial^2}{\partial \mu^2} + \frac{\cosh \mu}{\sinh \mu} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} + \frac{\cos \nu}{\sin \nu} \frac{\partial}{\partial \nu} \right. \right. \\
& \quad \left. \left. - \frac{\cosh^2 \mu - \cos^2 \nu}{\sinh^2 \mu \sin^2 \nu} (m - \frac{1}{2})^2 \right. \right. \\
& \quad \left. \left. + \frac{1}{2c^2 + E - V} \left[\left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \mu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \nu} \right) \right. \right. \right. \\
& \quad \quad \left. \left. - \left(\frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \nu} + \frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \mu} \right) (m - \frac{1}{2}) \right] \right] \psi_1^L \quad (6.60) \\
& \quad \left. - \frac{1}{2c^2 + E - V} \left[\left(\frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \nu} - \frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \mu} \right) (m + \frac{1}{2}) \right. \right. \\
& \quad \quad \left. \left. - \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \right] \psi_2^L \right\} \\
& \quad + (V - E) \psi_1^L = 0
\end{aligned}$$

and the lower equation becomes

$$\begin{aligned}
& -\frac{4f}{R^2(\cosh^2 \mu - \cos^2 \nu)} \times \\
& \quad \left\{ -\frac{1}{2c^2 + E - V} \left[\left(\frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \nu} - \frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \mu} \right) (m - \frac{1}{2}) \right. \right. \\
& \quad \quad \left. \left. + \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \nu} - \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \mu} \right) \right] \psi_1^L \right. \\
& \quad \left. + \frac{1}{2c^2 + E - V} \left[\left(+\frac{\cos \nu}{\sin \nu} \frac{\partial V}{\partial \nu} + \frac{\cosh \mu}{\sinh \mu} \frac{\partial V}{\partial \mu} \right) (m + \frac{1}{2}) \right. \right. \quad (6.61) \\
& \quad \quad \left. \left. + \left(\frac{\partial V}{\partial \mu} \frac{\partial}{\partial \mu} + \frac{\partial V}{\partial \nu} \frac{\partial}{\partial \nu} \right) \right] \psi_2^L \right. \\
& \quad \left. + \left[\frac{\partial^2}{\partial \mu^2} + \frac{\cosh \mu}{\sinh \mu} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} + \frac{\cos \nu}{\sin \nu} \frac{\partial}{\partial \nu} \right. \right. \\
& \quad \quad \left. \left. - \frac{\cosh^2 \mu - \cos^2 \nu}{\sinh^2 \mu \sin^2 \nu} (m + \frac{1}{2})^2 \right] \psi_2^L \right\} \\
& \quad + (V - E) \psi_2^L = 0
\end{aligned}$$