

QMC Workshop 2021

Spin-Orbit Coupling in Quantum Monte Carlo

Week 8 / 23 November 2021

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https://github.com/QMCPACK/qmc_workshop_2021

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Relativistic Electronic Structure

In order to introduce relativistic effects, one must use the Dirac-Coulomb Hamiltonian (scalar and spin-orbit interactions)

$$H = \sum_i [-ic(\alpha \cdot \nabla)_i + \beta c^2] - \sum_{iI} \frac{Z_I}{r_{iI}} + \sum_{i < j} \frac{1}{r_{ij}}$$

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

The corresponding wave functions are 4-component spinors

Directly solving this equation implicitly includes relativistic effects, which can have a significant impact on the material properties

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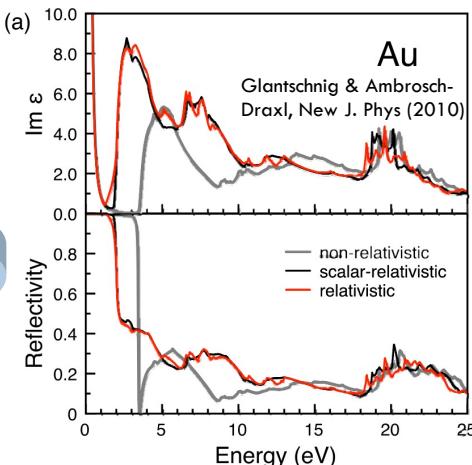
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Gold's color



Relativistic Electronic Structure

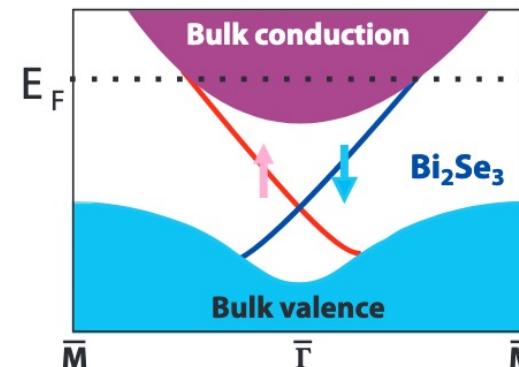
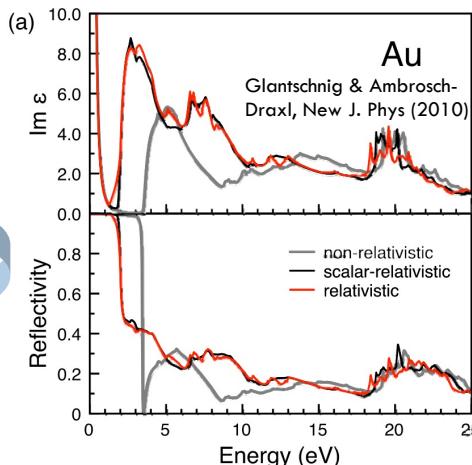
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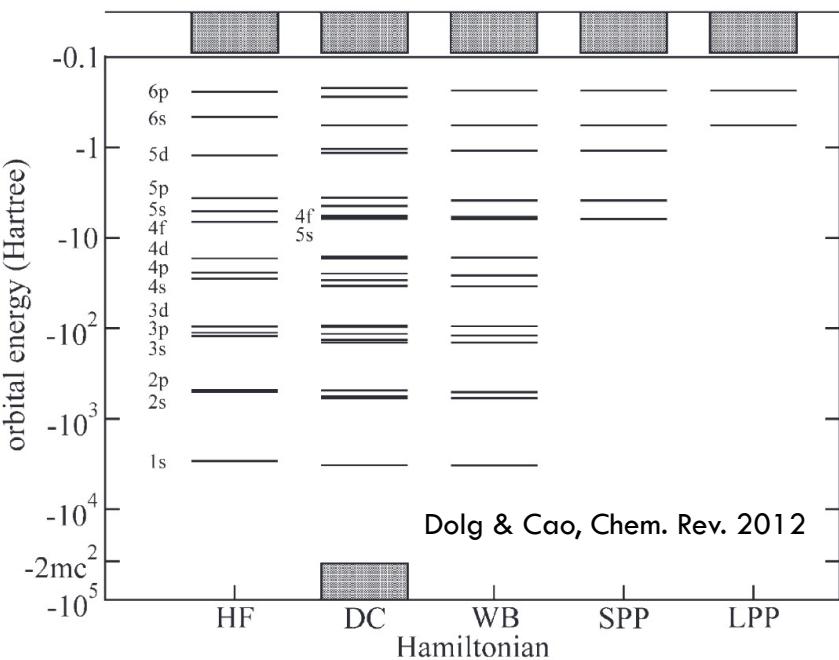


Topological insulators, where SOC can split the surface states

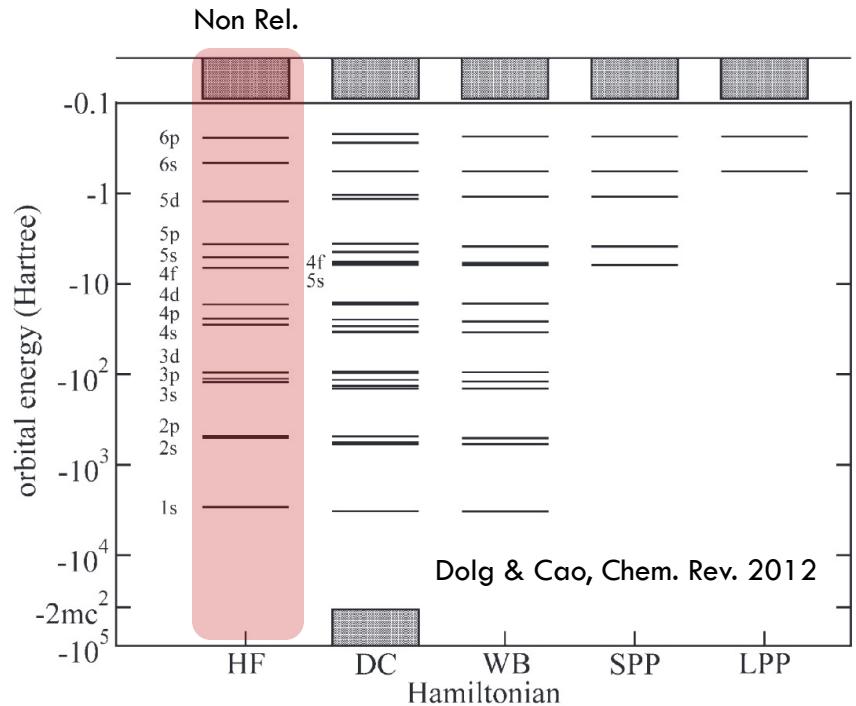
Hasan & Moore, Annu. Rev. Condens. Matter Phys. (2011)

For more interesting examples, see Pyykkö,
Annual Rev. Phys. Chem. (2012)

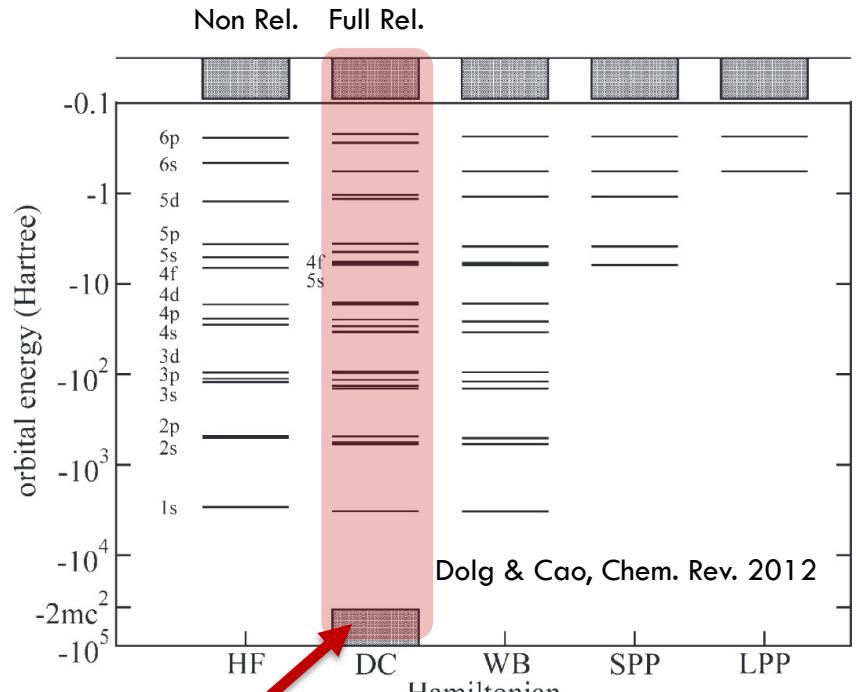
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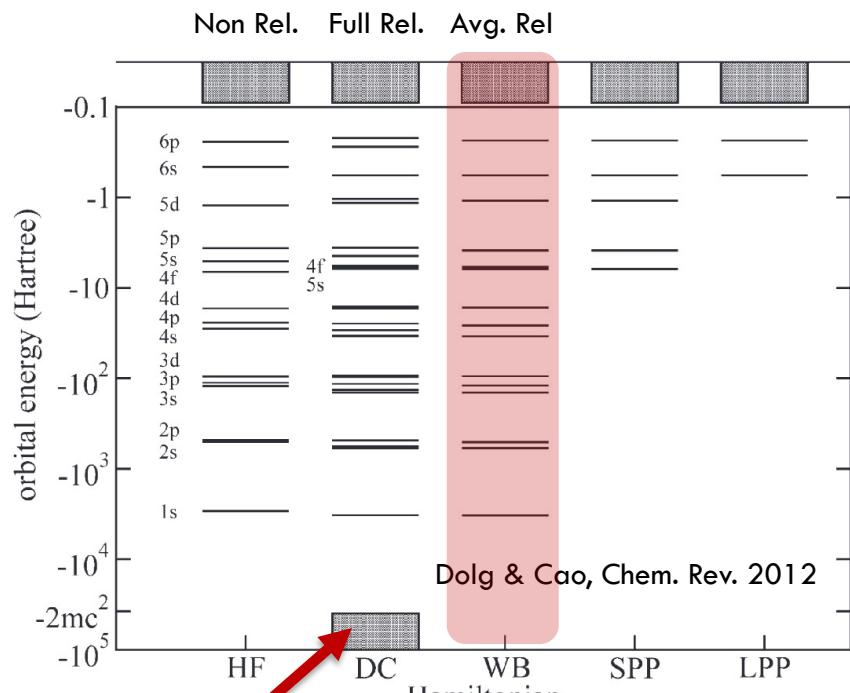


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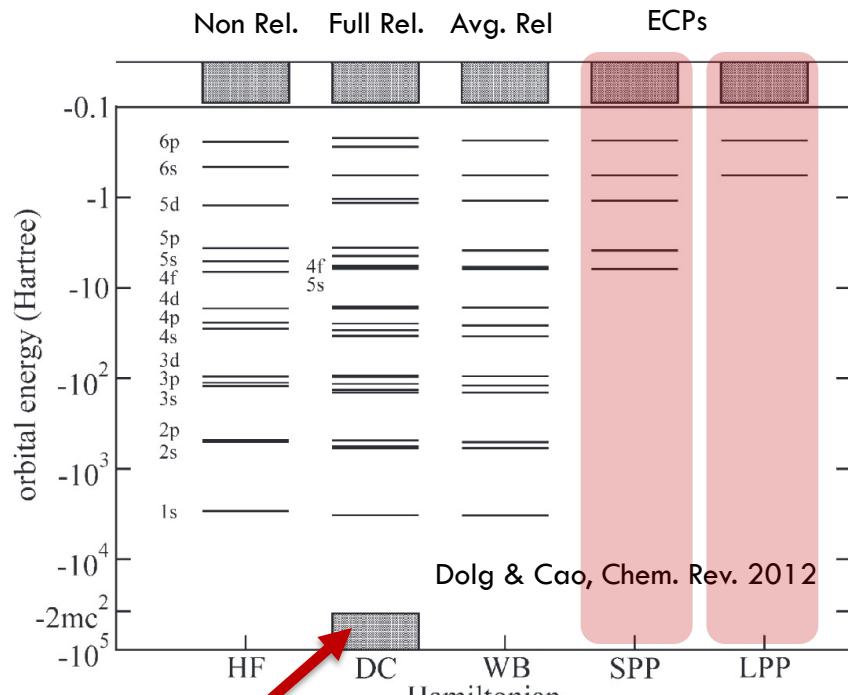
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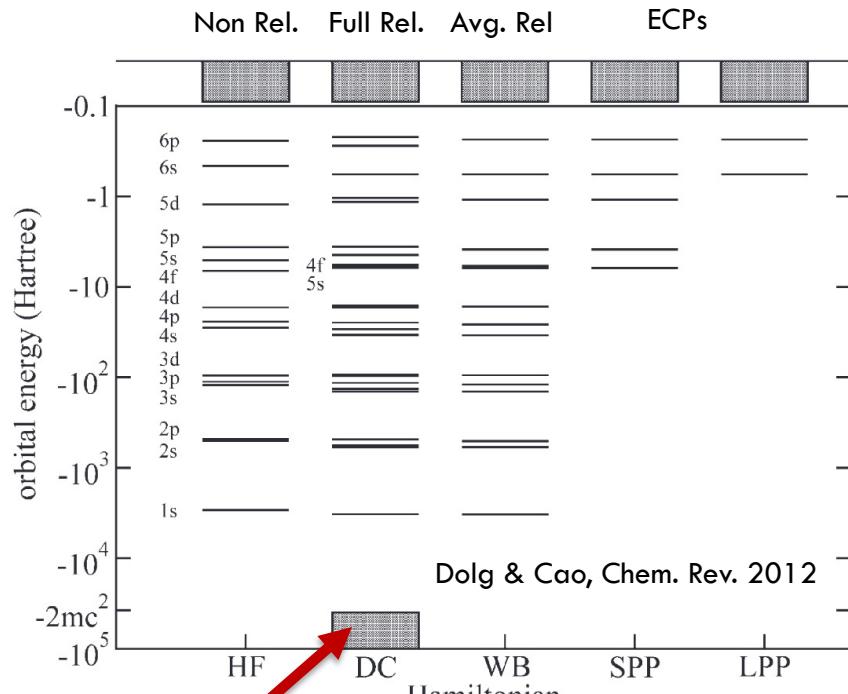
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DMC is a projector method → obtains lowest energy state of the Hamiltonian.

A DMC method for the Dirac Equation would need to stabilize against the low energy positronic states



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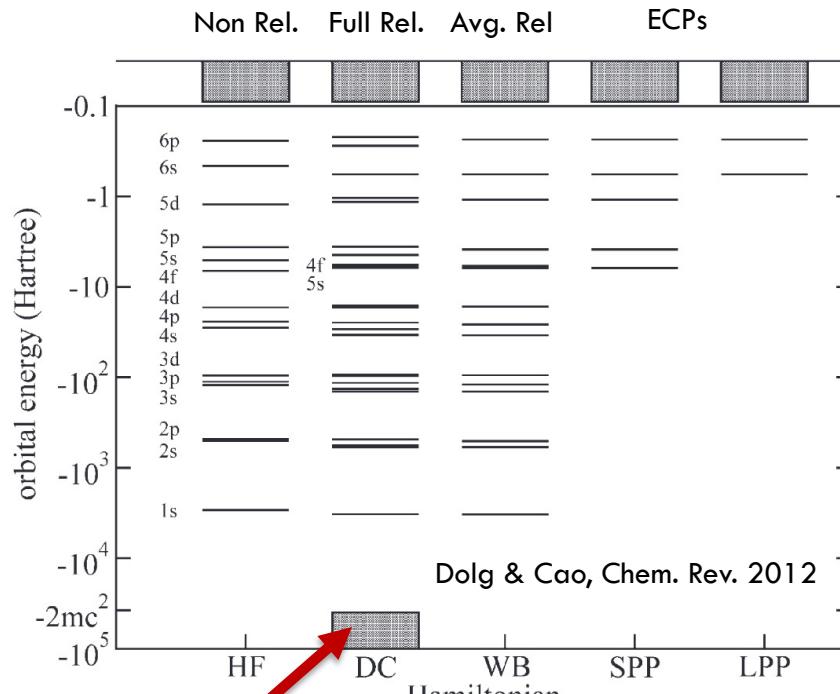
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Assuming we could stabilize for the electronic solution, there would still be significant scaling problems with the atomic number. (recall all-electron DMC is $Z^{5.5-6.5}$).

- Core electrons dominate energy and fluctuations
- Core electrons move relativistically...very different timescales between core and valence

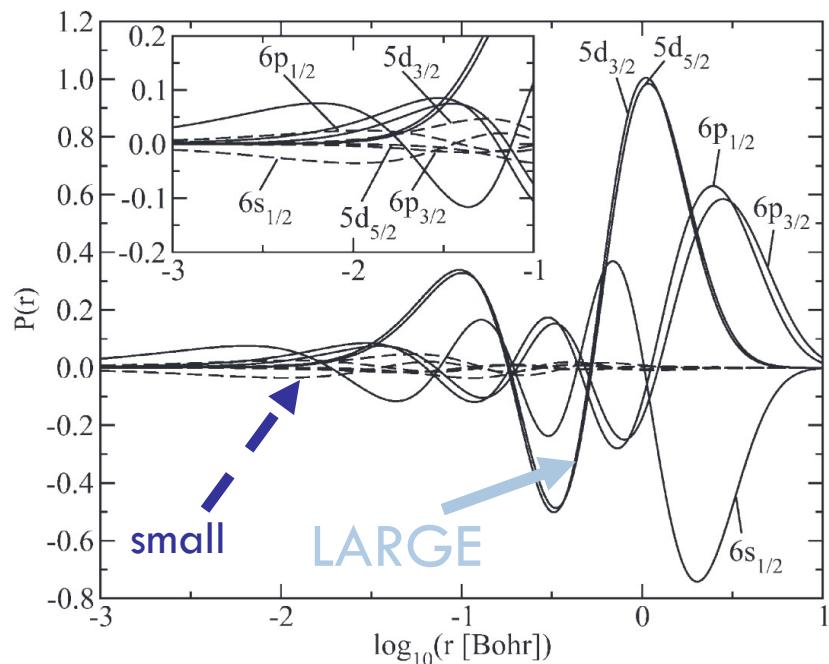
$$\langle v \rangle_{1s} \approx \frac{Z}{137} \cdot c \quad \text{e.g. Pb atom has } Z = 82, \text{ so the } 1s \text{ electron is moving 59.9\% the speed of light!}$$



"positronic" spectrum for Dirac-Coulomb hamiltonian

How to include relativity without the Dirac equation?

Core electrons provide an effective potential for valence electrons, implies we should use effective core potentials to remove inert core electrons. Do we still need to use 4-component spinors?



M. Dolg and X. Cao, Chem. Rev. 112 (2012)

Valence 4-component spinors for the Pb atom (left). The spinors can be written as “large” and “small” components, which are each 2-component spinors.

Note that the “small” components are completely negligible for the orbitals that participate in the chemical bonding of Pb.

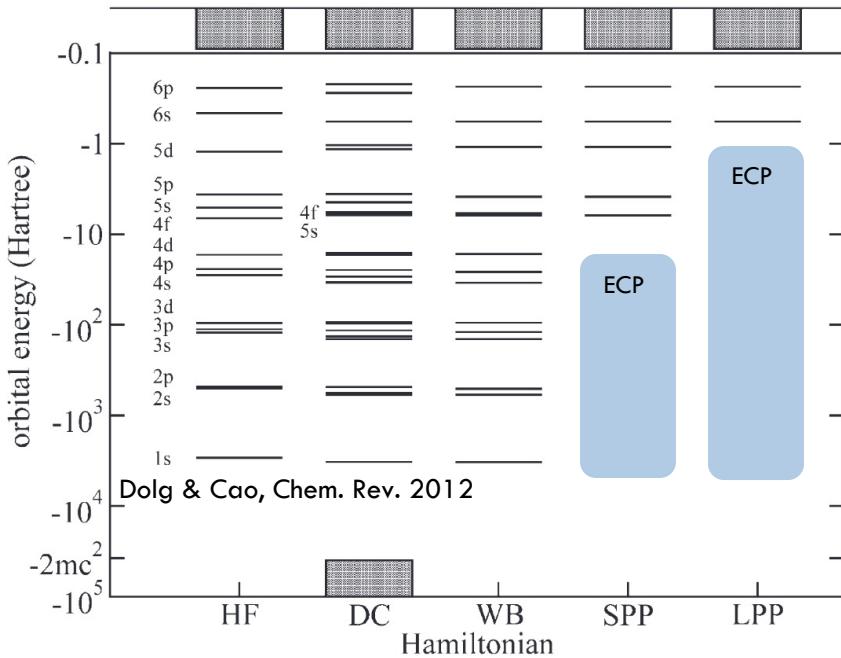
This implies we should be able to incorporate relativistic effects for the chemically active electrons, using an effective core potential and 2-component spinors

$$|\Psi\rangle = \begin{pmatrix} \Psi_L^{\uparrow} \\ \Psi_L^{\downarrow} \\ \Psi_S^{\uparrow} \\ \Psi_S^{\downarrow} \end{pmatrix} \xrightarrow{valence} \begin{pmatrix} \Psi_L^{\uparrow} \\ \Psi_L^{\downarrow} \end{pmatrix}$$

Relativistic Effective Core Potentials (RECPs)

In normal calculations, the ECP that replaces the core electrons is written using semi-local projectors over spherical harmonics.

$$W = \sum_{\ell, m_\ell} W_\ell(r) | \ell m_\ell \rangle \langle \ell m_\ell |$$



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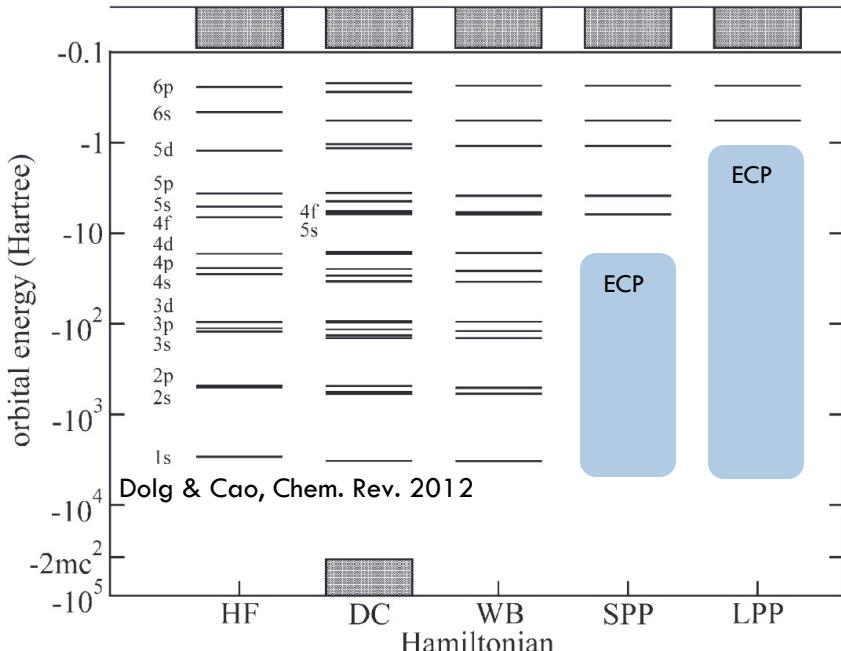
Recall that spin-orbit has an effective interaction

$$H_{SO} \propto \mathbf{L} \cdot \mathbf{S}$$

This implies that **L** and **S** aren't good quantum numbers. In this case, the total angular momentum **J** becomes a good quantum number.

$$W^{\text{avg. rel.}} = \sum_{\ell, m_\ell} W_\ell(r) |\ell m_\ell\rangle \langle \ell m_\ell|$$

$$\Rightarrow W^{\text{rel.}} = \sum_{\ell, j, m_j} W_{\ell j}(r) |\ell j m_j\rangle \langle \ell j m_j|$$



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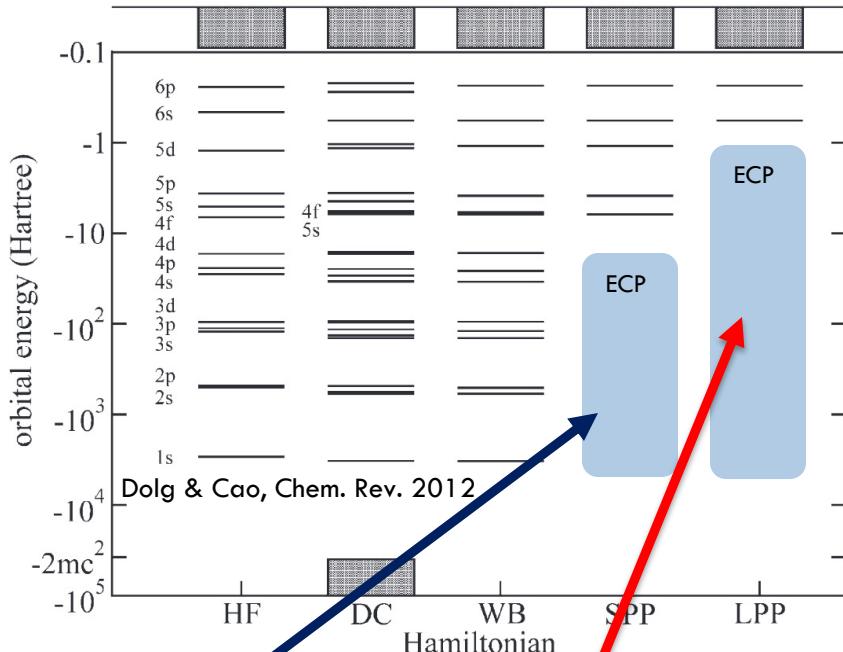
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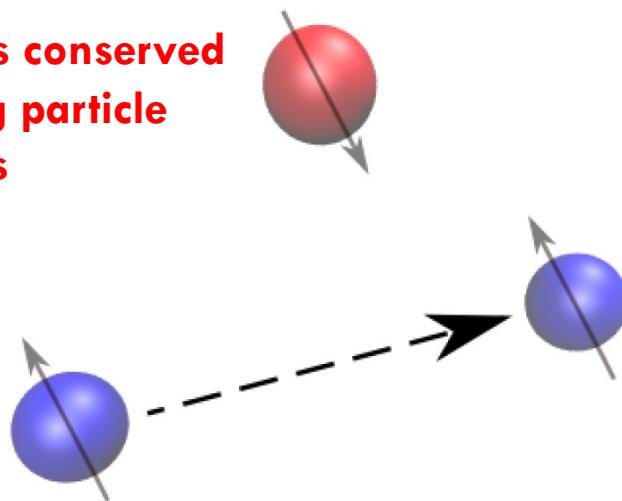


Small Core
Pseudopotential
removes these
states, and tries to
reproduce the
relativistic valence
spectrum

In standard QMC, since there are no spin interactions, spin commutes with the Hamiltonian. In this case, we can label each electron as “up” or “down” and that is preserved throughout the simulation.

$$[\mathcal{H}, S] = 0$$

**Spin is conserved
during particle
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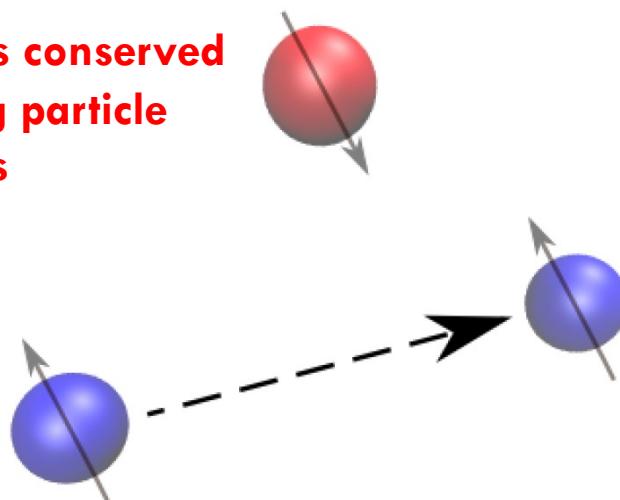
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With spin-orbit, the electron spin **isn't** conserved and will need to be sampled along with the spatial degrees of freedom.

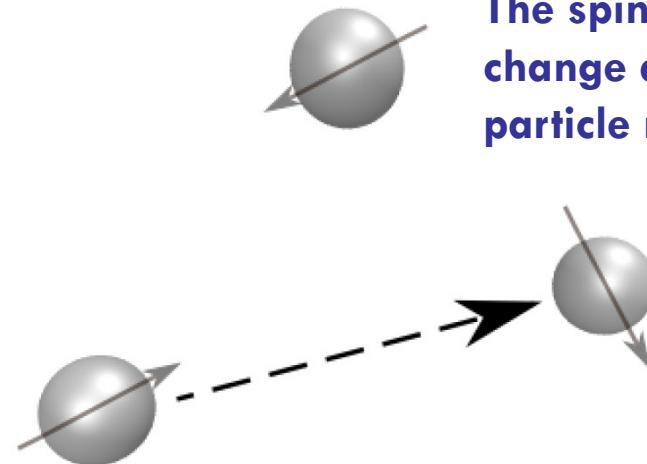
$$[\mathcal{H}, S] = 0$$

$$[\mathcal{H}, S] \neq 0$$

**Spin is conserved
during particle
moves**



**The spin can
change during
particle moves**



What do we need to implement in QMCPACK?

- ❖ Single particle spinors in QMCPACK, and converters from DFT codes
- ❖ Many-body wave function, constructed from these single particle spinors
- ❖ VMC/DMC algorithm that incorporates sampling of the spin degree of freedom
- ❖ Spin-orbit part of the Hamiltonian using relativistic ECPs

Implementation following Melton, Bennett, & Mitas, JCP, 114 (2016)

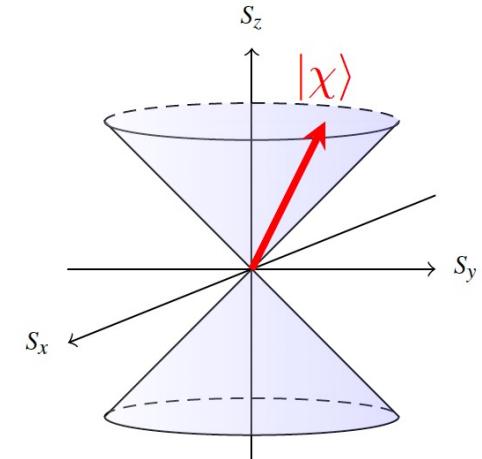
Single particle spinors

$$\langle \mathbf{x} | \psi \rangle = \phi^\uparrow(\mathbf{r}) \chi^\uparrow(s) + \phi^\downarrow(\mathbf{r}) \chi^\downarrow(s)$$

The general form of single particle spinors,
with $|\mathbf{x}\rangle = |\mathbf{r}\rangle |s\rangle$

Minimal representation

$$\begin{aligned}\langle s | \chi^\uparrow \rangle &= \chi^\uparrow(s) = \delta_{s,1} & s = \pm 1 \\ \langle s | \chi^\downarrow \rangle &= \chi^\downarrow(s) = \delta_{s,-1}\end{aligned}$$



With this representation, we have to sample the 2^N possible configurations discretely.
In the Monte Carlo sampling, a discrete change in an spin value could lead to a
large energy change → increases the E_L fluctuations

This can become inefficient with large N. Can we find an alternative representation?

Single particle spinors

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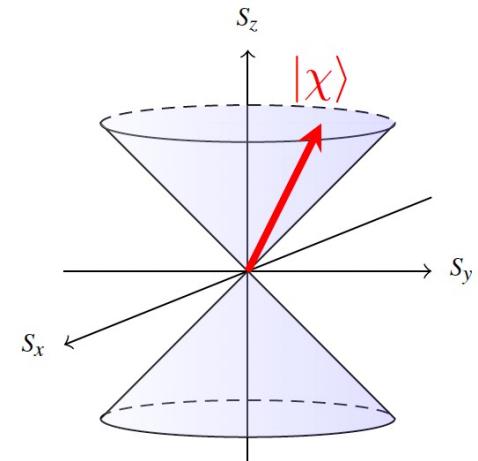
Continuous representation

$$\begin{aligned} \langle s | \chi^\uparrow \rangle &= \chi^\uparrow(s) = e^{is} & s \in [0, 2\pi) \\ \langle s | \chi^\downarrow \rangle &= \chi^\downarrow(s) = e^{-is} \end{aligned}$$

$$\langle \chi^\beta | \chi^\alpha \rangle = \int_0^{2\pi} \frac{ds}{2\pi} \langle \chi^\beta | s \rangle \langle s | \chi^\alpha \rangle = \delta_{\beta,\alpha}$$

Continuous representation preserves the properties of the spin states

With a continuous representation, the spin variable can be sampled in the same way the spatial variables are. Monte Carlo sampling is efficient, simply changes $\mathbf{R} \in \mathbb{R}^{3N} \Rightarrow \mathbf{X} \in \mathbb{R}^{4N}$



Where to get single-particle spinors?

$$\psi_i(\mathbf{r}_j, s_j) = \phi_i^\uparrow(\mathbf{r}_j)e^{is_j} + \phi_i^\downarrow(\mathbf{r}_j)e^{-is_j}$$

Atoms and Molecules

P program
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D direct
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R relativistic
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C calculations



DIRAC is used to study relativistic quantum chemistry.

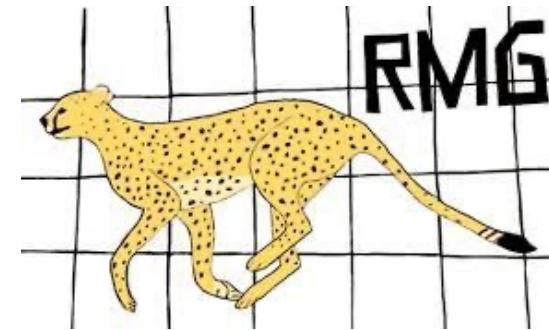
Can do non-relativistic, 2-component ECPs, 2-component all-electron, full 4-component treatments.

HF, COSCI, CISD, FCI, MP2, CCSD, and DFT

Support provided by `convert4qmc` in QMCPACK. More on this later



Solid State Materials



Quantum Espresso and RMGDFT can provide DFT spinors for 2-component calculations with ECPs

Quantum Espresso can generate orbitals using a new executable `convertpw4qmc`

RMGDFT directly generates the spinors for us. Use RMG input option `write_qmcpack_restart = "true"`

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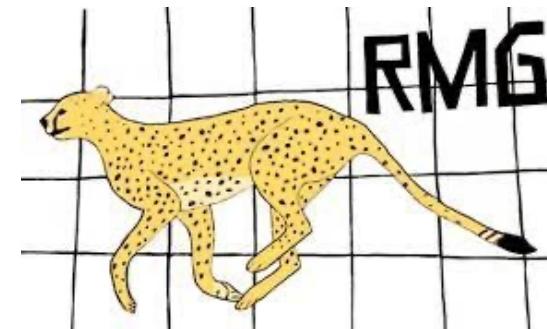
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Many-body wave function

$$\Psi_T(\mathbf{R}) = e^{J(\mathbf{R})} \sum_{\alpha} c_{\alpha} \det_{\alpha}^{\uparrow} \left[\dots, \phi_i^{\uparrow}(\mathbf{r}_j), \dots \right] \det_{\alpha}^{\downarrow} \left[\dots, \phi_k^{\downarrow}(\mathbf{r}_l), \dots \right]$$

 Change from orbitals $\{\phi_i^{\uparrow/\downarrow}(\mathbf{r}_j)\}$ to spinors $\{\psi_i(\mathbf{r}_j, s_j)\}$

$$\Psi_T(\mathbf{X}) = e^{J(\mathbf{R})} \sum_{\alpha} c_{\alpha} \det \left[\dots, \psi_i(\mathbf{r}_j, s_j), \dots \right]$$

Using spinors to construct a many-body wave function, there is no longer a separation of up and down determinants. Only one large determinant built from all the single particular spinors

Notice that the single particle spinors $\psi_i(\mathbf{r}_j, s_j) = \phi_i^{\uparrow}(\mathbf{r}_j)e^{is_j} + \phi_i^{\downarrow}(\mathbf{r}_j)e^{-is_j}$ are inherently complex, and therefore the full wave function is complex. For complex wave functions, the normal fixed-node approximation doesn't apply

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Fixed-Phase Approximation

For $\Psi(\mathbf{X}) \in \mathbb{C}$, the Fixed-Node approximation no longer applies

Let $\Psi(\mathbf{X}) = \rho(\mathbf{X}) \exp [i\Phi(\mathbf{X})]$, with *amplitude* ρ and *phase* Φ

Imaginary time Schrödinger equation \Rightarrow

$$\begin{aligned} -\frac{\partial \rho}{\partial \tau} &= \left[-\frac{1}{2} \nabla^2 + V + \frac{1}{2} |\nabla \Phi|^2 \right] \rho \\ -\frac{\partial \Phi}{\partial \tau} &= \left[-\frac{1}{2} \nabla^2 + \frac{\nabla \rho \cdot \nabla}{\rho} \right] \Phi \end{aligned}$$

Note that the amplitude is always positive, i.e. no sign structure

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$$\Psi_T(\mathbf{X}) \in \mathbb{R}$$

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Note: If you've run the solid examples with arbitrary twists, you've already used the FP approximation

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Diffusion Monte Carlo with Dynamic Spins

$$|\Psi_0\rangle \propto \lim_{\tau \rightarrow \infty} \exp [-\tau \mathcal{H}] |\Psi_T\rangle \quad E_0 = \lim_{\tau \rightarrow \infty} \frac{\langle \Psi(\tau) | \mathcal{H} | \Psi_T \rangle}{\langle \Psi(\tau) | \Psi_T \rangle}$$

$$\langle \mathbf{X}' = (\mathbf{R}', \mathbf{S}') | \Psi^{(n+1)} \rangle = \int d\mathbf{X} G(\mathbf{X} \rightarrow \mathbf{X}'; \tau) \langle \mathbf{X} | \Psi^{(n)} \rangle \quad \text{Imaginary time evolution in integral form}$$

Modification to the Greens function

$$G(\mathbf{X} \rightarrow \mathbf{X}'; \tau) \propto G(\mathbf{R} \rightarrow \mathbf{R}'; \tau) \exp (-|\mathbf{S}' - \mathbf{S} - \tau_s \mathbf{v}_s(\mathbf{S})|^2 / 2\tau_s)$$

Standard Drift/Diffusion and
Branching Greens Functions.
Only acts on particle positions

Drift/Diffusion Greens
function for the collective spin
variables

Relativistic ECPs

$$W^{\text{REP}} = \sum_{\ell,j,m_j} W_{\ell j}(r) |\ell j m_j\rangle \langle \ell j m_j|$$

Rather than work directly with the spin spherical harmonics projectors, in QMCPACK we decouple the ECP into an averaged relativistic effective potential (AREP) and a spin-orbit relativistic effective potential.

The AREP looks just like our normal pseudopotentials, and the SOREP contains the spin-orbit part of the Hamiltonian.

$$W^{\text{REP}} = W^{\text{AREP}} + W^{\text{SOREP}}$$

$$W^{\text{AREP}} = W_L(r) + \sum_{\ell,m} W_{\ell}^{\text{AREP}}(r) |\ell m\rangle \langle \ell m|$$

$$W^{\text{SOREP}} = \sum_{\ell} W_{\ell}^{\text{SOREP}}(r) \sum_{m,m'} |\ell m\rangle \langle \ell m| \vec{\ell} \cdot \vec{s} |\ell m'\rangle \langle \ell m'|$$

In QMCPACK, we include both the AREP and SOREP terms in the pseudopotential xml files

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Rather than work directly with the spin spherical harmonics projectors, in QMCPACK we decouple the ECP into an averaged relativistic effective potential (AREP) and a spin-orbit relativistic effective potential.

The AREP looks just like our normal pseudopotentials, and the SOREP contains the spin-orbit part of the Hamiltonian.

$$W^{\text{REP}} = W^{\text{AREP}} + W^{\text{SOREP}}$$

$$W^{\text{AREP}} = W_L(r) + \sum_{\ell,m} W_\ell^{\text{AREP}}(r) |\ell m\rangle \langle \ell m|$$

$$W^{\text{SOREP}} = \sum_{\ell} W_\ell^{\text{SOREP}}(r) \sum_{m,m'} |\ell m\rangle \langle \ell m| \vec{\ell} \cdot \vec{s} |\ell m'\rangle \langle \ell m'|$$

In QMCPACK, we include both the AREP and SOREP terms in the pseudopotential xml files

In the quantum chemistry community, REPs are typically specified as AREP + SOREP. For DFT potentials (Troullier-Martins, RKKJ, Kerker, etc.) these are typically specified as $W_{\ell j}^{\text{REP}}(r)$. There is a straightforward relation between the REP and AREP+SOREP

$$\begin{pmatrix} W_\ell^{\text{AREP}} \\ W_\ell^{\text{SOREP}} \end{pmatrix} = \begin{pmatrix} \frac{\ell+1}{2\ell+1} & \frac{\ell}{2\ell+1} \\ \frac{-2}{2\ell+1} & \frac{-2}{2\ell+1} \end{pmatrix} \begin{pmatrix} W_{\ell,j=\ell+1/2}^{\text{REP}} \\ W_{\ell,j=\ell-1/2}^{\text{REP}} \end{pmatrix}$$

Nitty gritty details for those interested

$$\frac{W^{\text{SO}}\Psi}{\Psi} = \sum_I \sum_i \int ds'_i \sum_{\alpha} w_{\alpha} \sum_{\ell} v_{\ell}^{\text{SO}}(r_{iI}) \frac{\Psi(\dots(\mathbf{q}_{iI}^{\alpha}, s'_i)\dots)}{\Psi(\dots(\mathbf{r}_i, s_i)\dots)} \sum_{m,m'} Y_{\ell,m}^*(\mathbf{r}_{iI}) Y_{\ell,m'}(r_{iI} \mathbf{u}^{\alpha}) \langle \ell m s_i | \ell \cdot \mathbf{s} | \ell m' s'_i \rangle$$

$$\mathbf{r}_{iI} = \mathbf{r}_i - \mathbf{R}_I$$

$$r_{iI} = |\mathbf{r}_{iI}|$$

$$\mathbf{q}_{iI}^{\alpha} = \mathbf{R}_I + r_{iI} \mathbf{u}^{\alpha}$$

This expression is evaluated in a similar way to normal pseudopotentials in QMC. We use quadrature points \mathbf{q} , and evaluate directly evaluate the wave function ratios. We use directly evaluate complex spherical harmonics rather than simplify into Legendre polynomials. Spin integral is performed using Simpsons rule

$$\Lambda = \langle \ell m s_i | \ell \cdot \mathbf{s} | \ell m' s'_i \rangle = \langle \ell m | \ell_{\mu} | \ell m' \rangle \langle s_i | s_{\mu} | s'_i \rangle$$

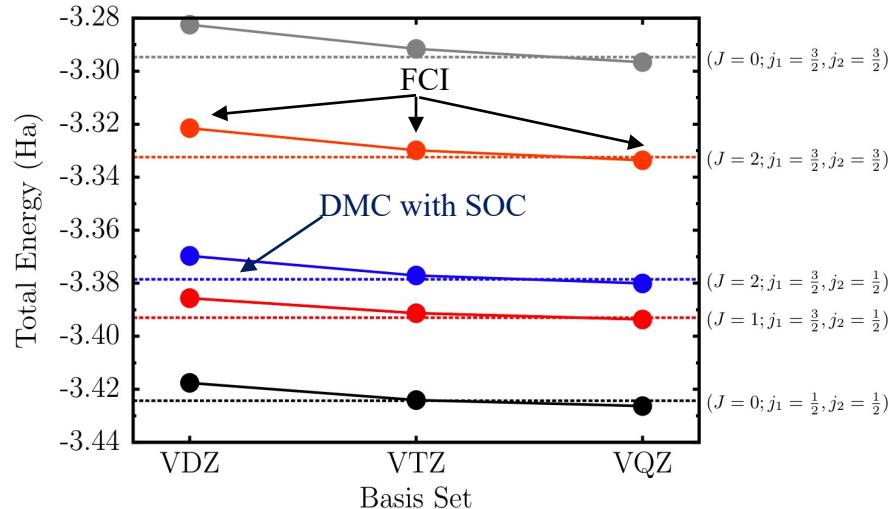
$$\langle s_i | s_{\mu} | s'_i \rangle = \begin{cases} \cos(s_i + s'_i), & \mu = x \\ \sin(s_i + s'_i), & \mu = y \\ i \sin(s_i - s'_i), & \mu = z \end{cases}$$

$$\langle \ell m | \ell_{\mu} | \ell m' \rangle = \begin{cases} \frac{1}{2} \left(\sqrt{\ell(\ell+1) - m'(m'+1)} \delta_{m,m'+1} + \sqrt{\ell(\ell+1) - m'(m'-1)} \delta_{m,m'-1} \right), & \mu = x \\ \frac{i}{2} \left(\sqrt{\ell(\ell+1) - m'(m'-1)} \delta_{m,m'-1} - \sqrt{\ell(\ell+1) - m'(m'+1)} \delta_{m,m'+1} \right), & \mu = y \\ m' \delta_{m,m'}, & \mu = z \end{cases}$$

The angular momentum matrix elements are straightforward. The spin matrix elements are obtained by expressing the spin operators into our continuous representation.

Examples for atomic / molecular systems

Total Energies of Pb with Large Core REP



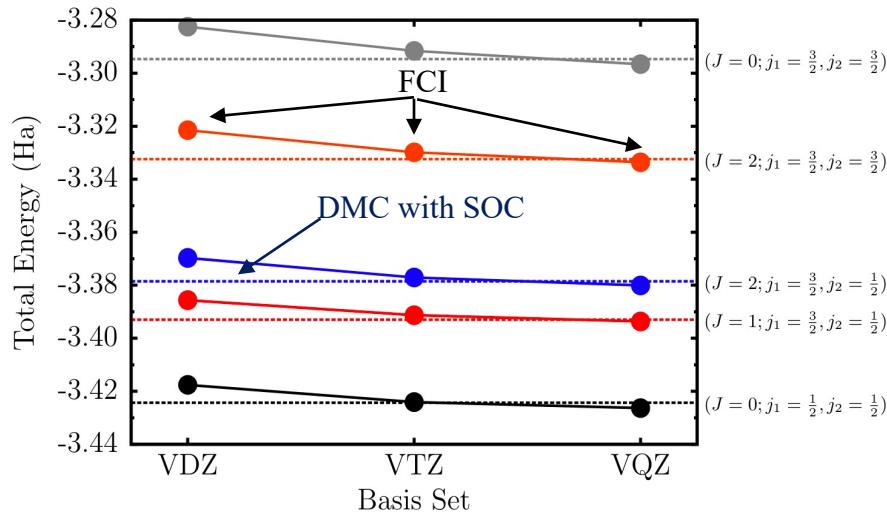
C.A. Melton *et al.*, PRA, 93, 2016

DMC comparison to exact FCI calculations for the same Hamiltonian (i.e. same ECP for both FCI and DMC)

DMC is able to reproduce the the total energies and splittings for **all** excited states.

Examples for atomic / molecular systems

Total Energies of Pb with Large Core REP

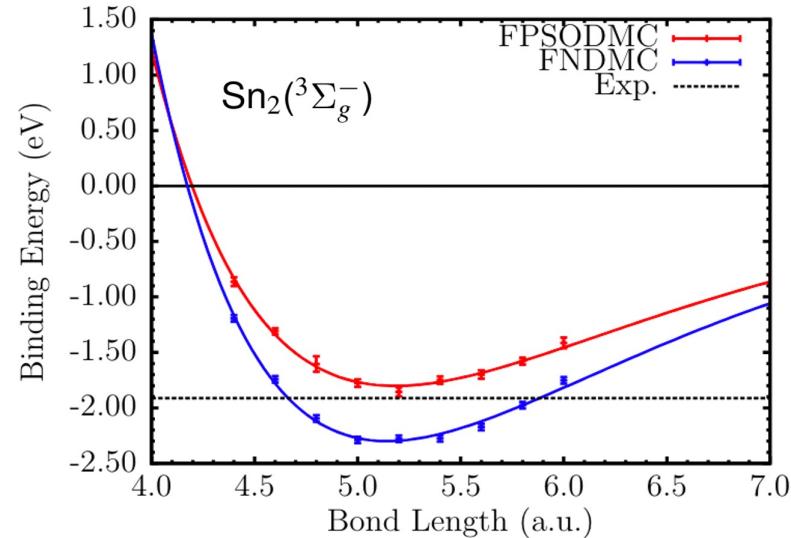


C.A. Melton *et al.*, PRA, 93, 2016

DMC comparison to exact FCI calculations for the same Hamiltonian (i.e. same ECP for both FCI and DMC)

DMC is able to reproduce the the total energies and splittings for **all** excited states.

Binding energy of Sn₂ impact of SOC



C.A. Melton *et al.*, JCP, 144, 2016

Comparison between DMC both with and without SOC.

Note that standard DMC would overbind the Sn₂ molecule by roughly 0.5 eV if SOC is neglected. DMC with SOC agrees with experiment

Summary

- Relativistic effects such as spin-orbit are extremely important for material properties with heavy elements. Until now, QMC methods have not been able to incorporate these effects. QMCPACK now has all the necessary ingredients to perform optimization, VMC, and DMC with spin-orbit included.
- Spin-orbit coupling can be conveniently incorporated into QMC through the use of relativistic pseudopotentials and two component spinors. Electrons also carry an additional spin degree of freedom which we sample.
- QMCPACK has interfaces to DIRAC for relativistic quantum chemistry applications and both Quantum Espresso and RMGDFT for solid state applications

Questions?

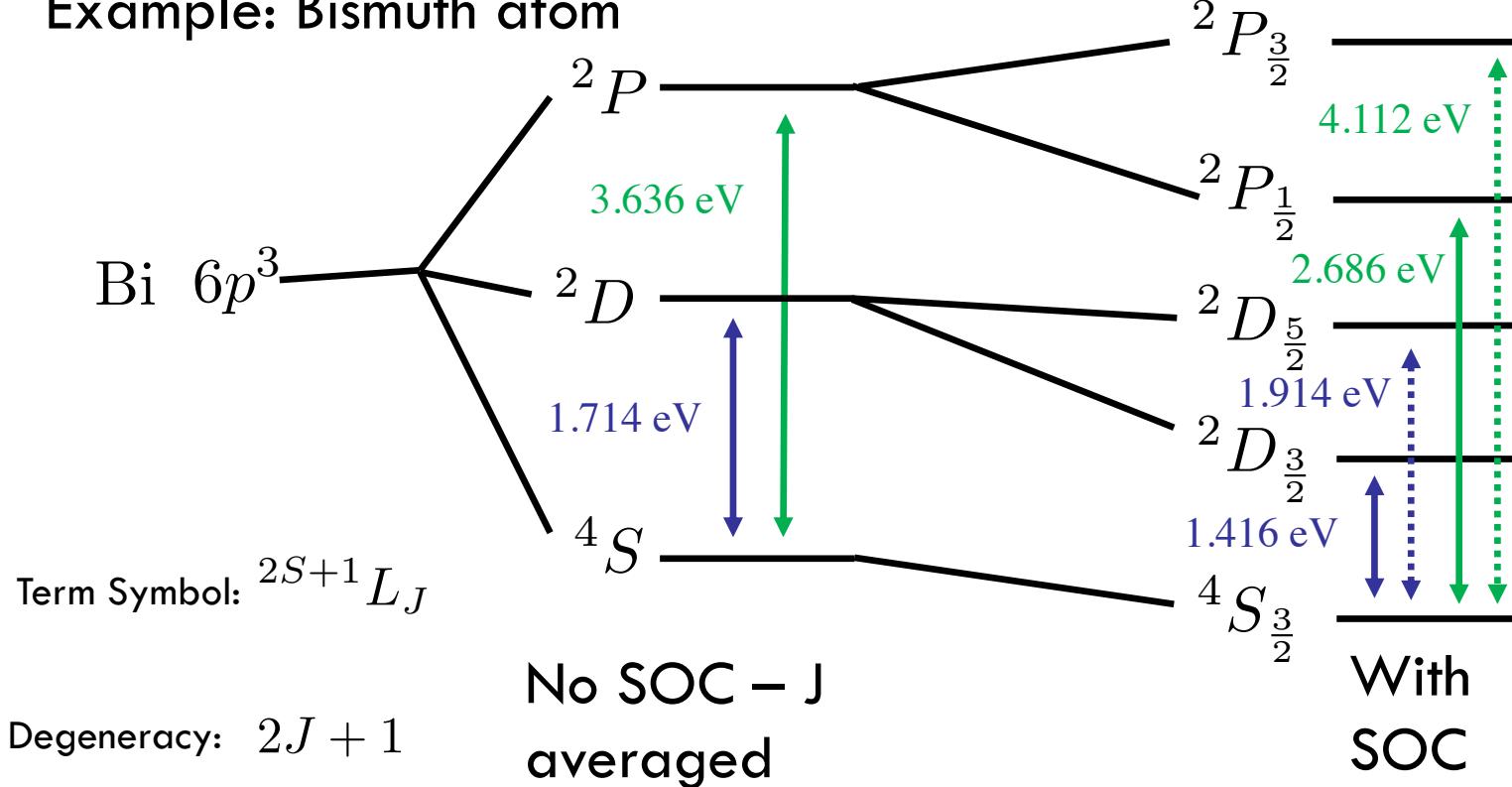
Hands on: Bi atom with DIRAC and QMCPACK

https://github.com/QMCPACK/qmc_workshop_2021/blob/master/week8_spin-orbit_qmc/

See the README.rst for a detailed walkthrough input/output files

Note: In the workshop image, please do a `git pull`. An update to the converter used in this hands-on session was pushed after the final image was made.

Example: Bismuth atom



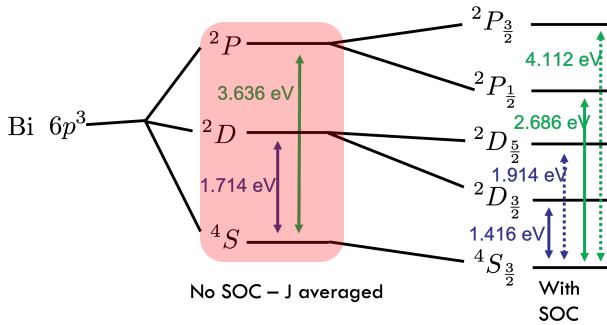
[NIST Atomic Spectra Database](#)

QMC Workshop 2021

Example 1: Spin-averaged states of Bismuth

DIRAC uses an average-of-configurations SCF calculation to solve open shell atoms.

For non-spin-orbit calculations, these are averaged over the standard p states



Need to specify open shell active space:

3 p electrons in $\{p_x^{\uparrow/\downarrow}, p_y^{\uparrow/\downarrow}, p_z^{\uparrow/\downarrow}\} \Rightarrow \binom{6}{3} = 20$ total determinants

SCF to obtain orbitals that minimize the average energy over the 20 determinants

$$E_{\text{AOC}} = \frac{1}{N_{\text{det}}} \sum_{i=1}^{N_{\text{det}}} \langle \Phi_i | H | \Phi_i \rangle$$

Resolve the open-shell states using the determinant basis to get small CI expansions.

Complete Open Shell CI (COSCI)

$$|\Psi_n\rangle = \sum_{i=1}^{N_{\text{det}}} c_i^n |\Phi_i\rangle$$

These represent the 20 possible states for the ⁴S, ²D, ²P terms

Example 1: Spin-averaged states of Bismuth

```
INTGRL
Bi
Bi STU ecp
C 1
  83. 1
Bi 0.000000 0.00000000 0.00000000
LARGE EXPLICIT 4 1 1 1 1
f 13 0
798.633
95.0023
21.2520
13.2919
8.31210
5.19476
1.99972
0.962271
0.356026
0.168327
0.0784
0.073265
0.0297
f 12 0
19.2259
12.2778
7.53421
2.14984
1.13036
0.566778
0.4469
0.273169
0.117769
0.0743
0.049384
0.0276
f 9 0
65.8224
13.6908
7.09591
2.52998
1.34866
0.682558
0.327714
0.1386
0.0488
f 2 0
0.3164
0.1188
ECP 76 5 6
3
1 40.00000 5.0
3 38.50000 200.0
2 40.00000 -74.796
2
2 1.994153 35.755622
2 0.242086 -0.484113
4
2 0.896039 2.688441
2 0.875463 5.715603
2 0.262580 -0.171255
2 0.232846 -0.150845
2
2 0.779775 4.060445
2 0.739216 5.980282
2
2 0.987519 -2.644657
2 0.959987 -3.373825
FINISH
```

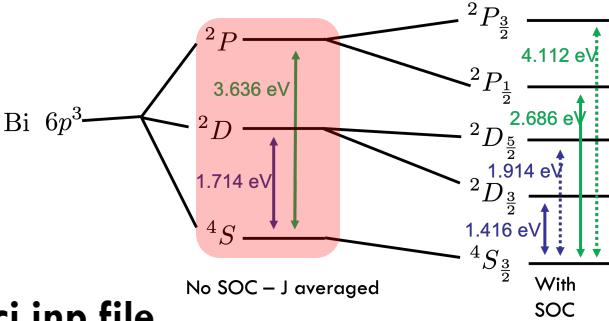
Bi.mol file

Specify geometry

Specify basis set
(here uncontracted)

Specify the ECP. Here
using a smoothed
Stuttgart ECP

```
**DIRAC
.WAVE FUNCTION
.ANALYZE
**HAMILTONIAN
.ECP
**INTEGRALS
*READIN
.UNCONTRACT
**WAVE FUNCTION
.RESOLVE
.SCF
*SCF
.CLOSED SHELL
2 0
.OPEN SHELL
1
3/0,6
.EVCCNV
1.0d-05
**ANALYZE
.PRIVEC
.MULPOP
*PRIVEC
.AOLAB
.VECPRI
1..oo
1..oo
.PRINT
1
*MULPOP
.AOLAB
.VECPOP
1..oo
1..oo
.PRINT
1
**GENERAL
.PCMOUT
*END OF
&GOSCIIP IPRNT=5 &END
```



cosci.inp file

Specify we calculate
wavefunction and
analyze

Specify the atomic
configuration

Specify we print
all the orbitals.
Required for
QMCPACK
converter

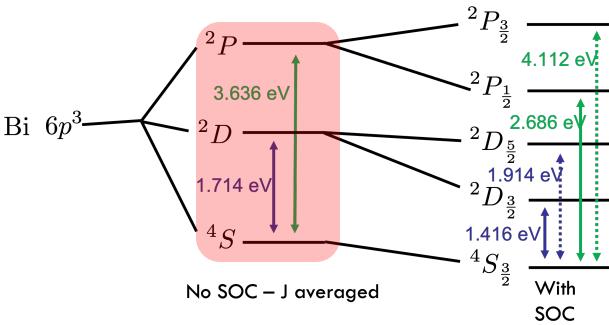
To run:

```
|--> pam-dirac --inp=cosci.inp --mol=Bi.mol
```

Detailed description of
the inputs on the [github](#)
page!

Example 1: Spin-averaged states of Bismuth

Configuration	Term	J	Level (eV)	Uncertainty (eV)	Landé-g	Leading percentages	Reference
$6p^3$	$^4S^o$	$3/2$	0.0000000				L6416
	term		0				
$6p^3$	$^2D^o$	$3/2$	1.4157804		1.225		L6416
		$5/2$	1.9140062		1.20		L6416
	term		1.7147159				
$6p^3$	$^2P^o$	$1/2$	2.6856111		0.667		L6416
		$3/2$	4.1119118				L6416
	term		3.6364782				



[NIST Atomic Spectra Database](#)

Energy eigenvalues in atomic units

Level	Rel eigenvalue	Abs eigenvalue	Total Energy	Degeneracy
1	0.000000000	-1.750400036742	-5.271133025983	(4 *)
2	0.0570123148	-1.693387721973	-5.214120711214	(10 *)
3	0.0950205246	-1.655379512127	-5.176112501368	(6 *)

Total average:

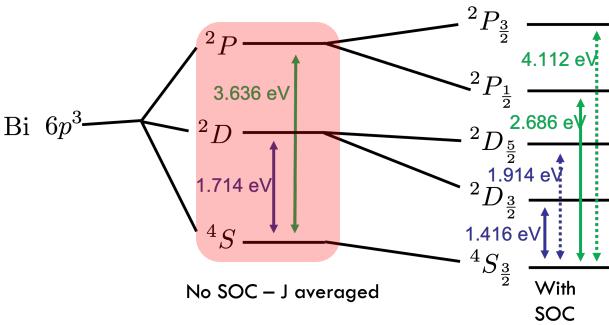
-5.2141207112

$$E_{\text{AOC}} = \frac{1}{N_{\text{det}}} \sum_{i=1}^{N_{\text{det}}} \langle \Phi_i | H | \Phi_i \rangle$$

cosci_Bi.out

Example 1: Spin-averaged states of Bismuth

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6p ³	⁴ S°	3/2	0.0000000				L6416
	term		0				
6p ³	² D°	3/2	1.4157804		1.225		L6416
		5/2	1.9140062		1.20		L6416
	term		1.7147159				
6p ³	² P°	1/2	2.6856111		0.667		L6416
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NIST Atomic Spectra Database

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Total average:		-5.2141207112			

cosci_Bi.out

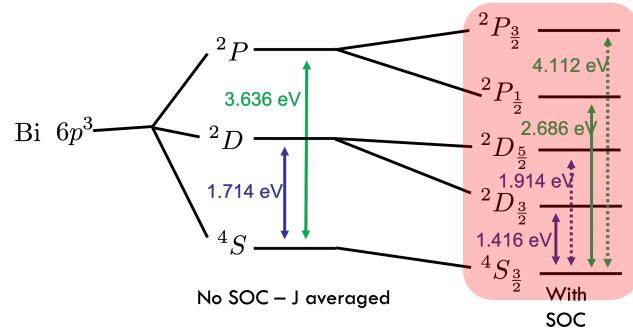
$$E_{\text{AOC}} = \frac{1}{N_{\text{det}}} \sum_{i=1}^{N_{\text{det}}} \langle \Phi_i | H | \Phi_i \rangle$$

State	COSCI Energy (eV)	Error w/ Expt. (eV)
⁴ S	0.00000	N/A
² D	1.55138	0.16333
² P	2.5856399	1.05084

Example 2: Spin-Orbit States of Bismuth

DIRAC uses an average-of-configurations SCF calculation to solve open shell atoms.

For spin-orbit calculations, these are averaged over the p states with j -quantum numbers



Need to specify open shell active space:

$$3 \text{ } p \text{ electrons in } \left\{ p_{3/2}^{m=\pm 1/2, \pm 3/2}, p_{1/2}^{m=\pm 1/2} \right\} \Rightarrow \binom{6}{3} = 20 \text{ total determinants}$$

SCF to obtain orbitals that minimize the average energy over the 20 determinants

$$E_{\text{AOC}} = \frac{1}{N_{\text{det}}} \sum_{i=1}^{N_{\text{det}}} \langle \Phi_i | H | \Phi_i \rangle$$

Resolve the open-shell states using the determinant basis to get small CI expansions.
Complete Open Shell CI (COSCI).

$$|\Psi_n\rangle = \sum_{i=1}^{N_{\text{det}}} c_i^n |\Phi_i\rangle$$

These represent the 20 possible states for the $^4S_{3/2}$, $^2D_{3/2}$, $^2D_{5/2}$, $^2P_{1/2}$, $^2P_{3/2}$ terms

Example 2: Spin-Orbit States of Bismuth

Configuration	Term	J	Level (eV)	Uncertainty (eV)	Landé-g	Leading percentages	Reference
6p ³	⁴ S°	³ / ₂	0.0000000				L6416
	term		θ				
6p ³	² D°	³ / ₂	1.4157804		1.225		L6416
		⁵ / ₂	1.9140062		1.20		L6416
	term		1.7147159				
6p ³	² P°	¹ / ₂	2.6856111		0.667		L6416
		³ / ₂	4.1119118				L6416
	term		3.6364782				

NIST Atomic Spectra Database

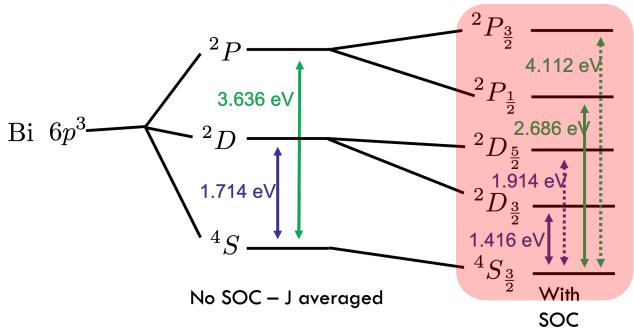
Energy eigenvalues in atomic units

Level	Rel eigenvalue	Abs eigenvalue	Total Energy	Degeneracy
1	0.000000000	-1.780162163308	-5.300947773703 (4 *
2	0.0566920241	-1.723470139197	-5.244255749591 (4 *
3	0.0782419737	-1.701920189567	-5.222705799962 (6 *
4	0.1142162781	-1.665945885253	-5.186731495648 (2 *
5	0.1627542231	-1.617407940163	-5.138193550557 (4 *

Total average:

-5.2221643043

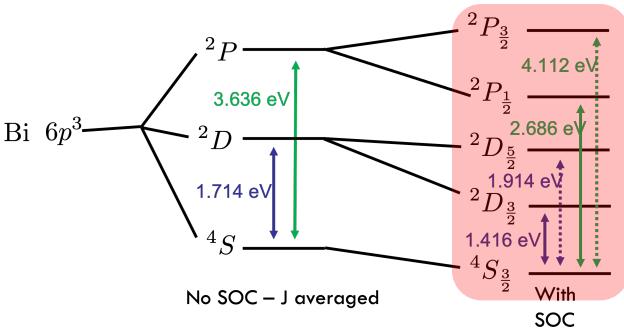
cosci_Bi.out



$$E_{\text{AOC}} = \frac{1}{N_{\text{det}}} \sum_{i=1}^{N_{\text{det}}} \langle \Phi_i | H | \Phi_i \rangle$$

Example 2: Spin-Orbit States of Bismuth

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		⁵ / ₂	1.9140062		1.20		L6416
	term		1.7147159				
6p ³	² P°	¹ / ₂	2.6856111		0.667		L6416
		³ / ₂	4.1119118				L6416
	term		3.6364782				



NIST Atomic Spectra Database

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5	0.1627542231	-1.617407940163	-5.138193550557	(4 *)
Total average:		-5.2221643043		

cosci_Bi.out

$$E_{\text{AOC}} = \frac{1}{N_{\text{det}}} \sum_{i=1}^{N_{\text{det}}} \langle \Phi_i | H | \Phi_i \rangle$$

$$|\Psi_n\rangle = \sum_{i=1}^{N_{\text{det}}} c_i^n |\Phi_i\rangle$$

State	COSCI Energy (eV)	Error w/ Expt. (eV)
4S _{3/2}	0.00000	N/A
2D _{3/2}	1.54266	-0.12688
2D _{5/2}	2.12907	-0.21506
2P _{1/2}	3.10798	-0.42237
2P _{3/2}	4.42876	-0.31685

Example 2: Spin-Orbit States of Bismuth

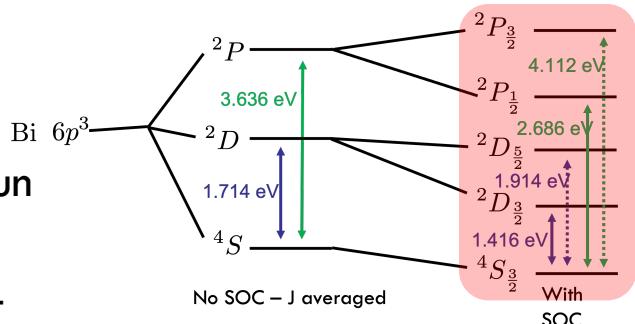
To generate the input files for QMCPACK, we simply need to run `convert4qmc` on the `cosci_Bi.out` files.

Note: We can use the spin-averaged or fully relativistic wavefunctions from DIRAC in QMCPACK. In this tutorial, we only look at the spin-orbit states

First, we test the converter by running a VMC calculation with no jastrow. This **should** reproduce the energies from COSCI

```
|> convert4qmc -dirac cosci_dirac.out -nojastrow -TargetState 0 -prefix state_0  
|> mpirun -np N qmcpack-complex state_0.qmc.in-wfn0j.xml | tee state_0.qmc.in-wfn0j.out
```

Population analysis for representation 1u					
The first 5 vectors are analyzed			norm	Re	Im
energy	det#	determinant	---	---	---
-5.30094777	1	110100	0.7371	-0.8586	0.0000
	2	110010	0.0416	0.2040	0.0000
	3	101001	0.0416	-0.2040	0.0000
	4	011001	0.0547	-0.2340	0.0000
	5	000111	0.1249	-0.3534	0.0000
Orb.	Orbital energy	Occupation			
1	-0.2636503417	0.8204			
2	-0.1928178379	0.8335			
3	-0.1928178379	0.0964			
4	-0.2636503417	0.8620			
5	-0.1928178379	0.1665			
6	-0.1928178379	0.2212			
Sum of occupations :			3.0000		



`cosci_Bi.out:`

```
cosci State Info  
-----  
Found 6 representations  
Representation: 1u with 5 states  
state# Energies and Ndets:  
0 -5.300947770000e+00 5  
1 -5.244255750000e+00 4  
2 -5.222705800000e+00 3  
3 -5.186731500000e+00 2  
4 -5.138193550000e+00 5  
Representation: -1u with 5 states  
state# Energies and Ndets:  
5 -5.300947770000e+00 5  
6 -5.244255750000e+00 4  
7 -5.222705800000e+00 3  
8 -5.186731500000e+00 2  
9 -5.138193550000e+00 5  
Representation: 3u with 4 states  
state# Energies and Ndets:  
10 -5.300947770000e+00 4  
11 -5.244255750000e+00 3  
12 -5.222705800000e+00 2  
13 -5.138193550000e+00 4  
Representation: -3u with 4 states  
state# Energies and Ndets:  
14 -5.300947770000e+00 4  
15 -5.244255750000e+00 3  
16 -5.222705800000e+00 2  
17 -5.138193550000e+00 4  
Representation: 5u with 1 states  
state# Energies and Ndets:  
18 -5.222705800000e+00 1  
Representation: -5u with 1 states  
state# Energies and Ndets:  
19 -5.222705800000e+00 1  
Saving wave function for target state 0
```

Example 2: Spin-Orbit States of Bismuth

Run the converter on all the unique states to generate VMC inputs and then run qmcpack.

DIRAC-COSCI

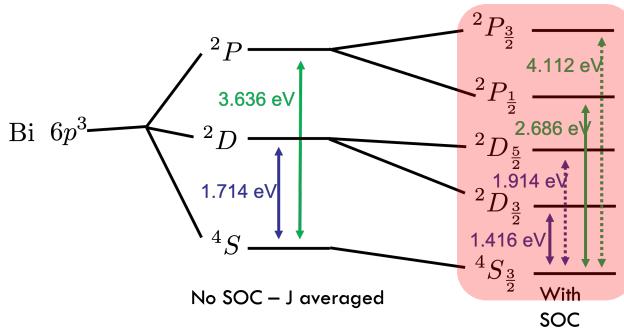
Energy eigenvalues in atomic units

Level	Rel eigenvalue	Abs eigenvalue	Total Energy	Degeneracy
1	0.0000000000	-1.780162163308	-5.300947773703	(4 *)
2	0.0566920241	-1.723470139197	-5.244255749591	(4 *)
3	0.0782419737	-1.701920189567	-5.222705799962	(6 *)
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5	0.1627542231	-1.617407940163	-5.138193550557	(4 *)

Total average: -5.2221643043

QMCPACK – VMC w/ no Jastrow

	LocalEnergy	Variance	ratio
state_0	series 0 -5.300973 +/- 0.000387	0.260264 +/- 0.003473	0.0491
state_1	series 0 -5.243824 +/- 0.004710	0.338262 +/- 0.068780	0.0645
state_2	series 0 -5.221590 +/- 0.002897	0.290984 +/- 0.021331	0.0557
state_3	series 0 -5.188029 +/- 0.003165	0.282325 +/- 0.010537	0.0544
state_4	series 0 -5.139926 +/- 0.002713	0.281456 +/- 0.013977	0.0548



Energies agree to within statistical error. This implies the converter worked and we have the correct wavefunctions.

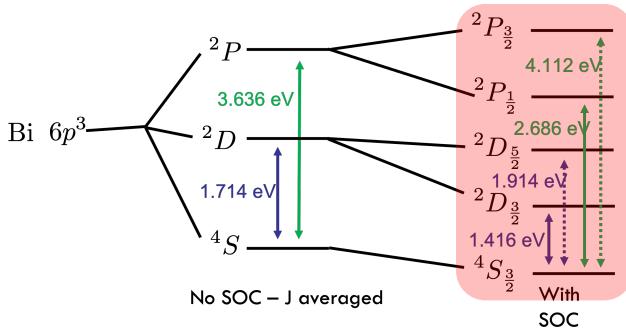
Now we can optimize jastrows and see if DMC improves the energies compared to experiment!

Example 2: Spin-Orbit States of Bismuth

Run the converter on all the unique states and run QMCPACK on the resulting files.

If you use convert4qmc without the `--nojastrow` flag, the input files will have optimization, VMC and DMC blocks

```
|> convert4qmc -dirac cosci_dirac.out -TargetState 0 -prefix qmc_state_0  
|> mpirun -np N qmcpack-complex qmc_state_0.qmc.in-wfj.xml | tee qmc_state_0.qmc.in-wfj.out
```



qmc_state_0.qmc.in-wfj.xml

Optimization blocks

```
<loop max="4">  
  <qmc method="linear" move="pbyp" checkpoint="-1">  
    <estimator name="LocalEnergy" hdf5="no"/>  
    <parameter name="warmupSteps">100</parameter>  
    <parameter name="blocks">20</parameter>  
    <parameter name="timestep">0.5</parameter>  
    <parameter name="walkers">1</parameter>  
    <parameter name="samples">1600</parameter>  
    <parameter name="substeps">4</parameter>  
    <parameter name="usedrift">no</parameter>  
    <parameter name="MinMethod">OneShiftOnly</parameter>  
    <parameter name="minwalkers">0.3</parameter>  
  </qmc>  
</loop>
```

VMC block

```
<qmc method="vmc" move="pbyp" checkpoint="-1">  
  <estimator name="LocalEnergy" hdf5="no"/>  
  <parameter name="warmupSteps">100</parameter>  
  <parameter name="blocks">200</parameter>  
  <parameter name="steps">50</parameter>  
  <parameter name="substeps">8</parameter>  
  <parameter name="timestep">0.5</parameter>  
  <parameter name="usedrift">no</parameter>  
  <!--Sample count should match targetwalker count for-->  
  <parameter name="samples">2048</parameter>  
</qmc>
```

DMC block

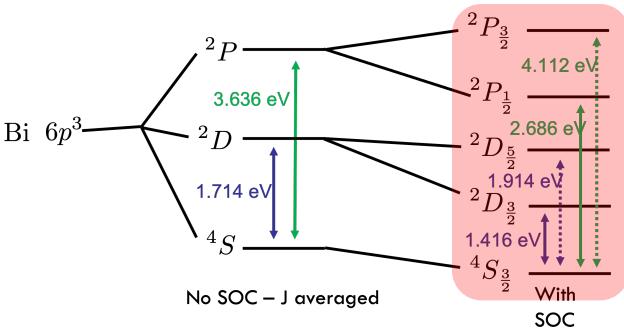
```
<qmc method="dmc" move="pbyp" checkpoint="20">  
  <estimator name="LocalEnergy" hdf5="no"/>  
  <parameter name="targetwalkers">2048</parameter>  
  <parameter name="reconfiguration">no</parameter>  
  <parameter name="warmupSteps">100</parameter>  
  <parameter name="timestep">0.0005</parameter>  
  <parameter name="steps">30</parameter>  
  <parameter name="blocks">1000</parameter>  
  <parameter name="nonlocalmoves">no</parameter>  
</qmc>
```

Example 2: Spin-Orbit States of Bismuth

For simplicity, only running the VMC/DMC on the $^4S_{3/2}$ and $^2P_{3/2}$ states

```
qmc_state_0 series 7
LocalEnergy      =      -5.3885 +/-    0.0012
Variance         =       0.0692 +/-    0.0039
Kinetic          =       1.650 +/-     0.011
LocalPotential   =      -7.038 +/-    0.012
ElecElec         =      2.8951 +/-    0.0014
LocaleCP          =     -10.6238 +/-   0.0064
NonLocalECP      =       0.755 +/-    0.012
LocalEnergy_sq   =      29.105 +/-    0.016
SOECP            =     -0.06416 +/-   0.00069
BlockWeight       =     61427.01 +/-   153.39
BlockCPU          =      211.65 +/-    3.74
AcceptRatio       =      0.993808 +/-  0.000034
Efficiency        =       1.05 +/-     0.00
TotalTime         =     38731.98 +/-   0.00
TotalSamples      =    11241143 +/-    0
```

```
qmc_state_4 series 7
LocalEnergy      =      -5.2417 +/-    0.0015
Variance         =       0.0848 +/-    0.0062
Kinetic          =       1.5424 +/-    0.0040
LocalPotential   =      -6.7841 +/-    0.0041
ElecElec         =      2.8001 +/-    0.0027
LocaleCP          =     -10.239 +/-    0.013
NonLocalECP      =       0.6044 +/-    0.0084
LocalEnergy_sq   =      27.560 +/-    0.017
SOECP            =      0.05038 +/-   0.00027
BlockWeight       =     61394.28 +/-   170.10
BlockCPU          =      207.33 +/-    3.07
AcceptRatio       =      0.993426 +/-  0.000027
Efficiency        =       0.39 +/-     0.00
TotalTime         =     70700.26 +/-   0.00
TotalSamples      =    20935448 +/-    0
```



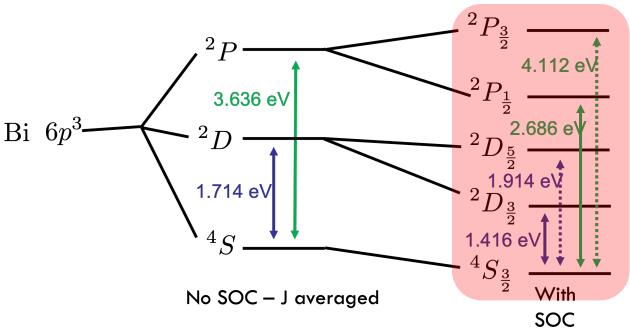
$$\begin{aligned}
 W^{\text{REP}} &= W^{\text{AREP}} + W^{\text{SOREP}} \\
 W^{\text{AREP}} &= W_L(r) + \sum_{\ell,m} W_\ell^{\text{AREP}}(r) |\ell m\rangle \langle \ell m| \\
 W^{\text{SOREP}} &= \sum_{\ell} W_\ell^{\text{SOREP}}(r) \sum_{m,m'} |\ell m\rangle \langle \ell m | \vec{\ell} \cdot \vec{s} | \ell m' \rangle \langle \ell m' |
 \end{aligned}$$

Example 2: Spin-Orbit States of Bismuth

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LocalPotential   =      -7.038 +/-    0.012
ElecElec         =      2.8951 +/-    0.0014
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```



$$\begin{aligned} W^{\text{REP}} &= W^{\text{AREP}} + W^{\text{SOREP}} \\ W^{\text{AREP}} &= W_L(r) + \sum_{\ell,m} W_\ell^{\text{AREP}}(r) |\ell m\rangle \langle \ell m| \\ W^{\text{SOREP}} &= \sum_{\ell} W_\ell^{\text{SOREP}}(r) \sum_{m,m'} |\ell m\rangle \langle \ell m | \vec{\ell} \cdot \vec{s} | \ell m' \rangle \langle \ell m' | \end{aligned}$$

$$E_{\text{DMC}}(^4S_{3/2}) = -5.3885(12) \text{ Ha}$$

$$E_{\text{DMC}}(^2P_{3/2}) = -5.2417(15) \text{ Ha}$$

$$\Delta_{\text{COSCI}}(^2P_{3/2} \rightarrow ^4S_{3/2}) = 4.43 \text{ eV}$$

$$\Delta_{\text{DMC}}(^2P_{3/2} \rightarrow ^4S_{3/2}) = 3.99(5) \text{ eV}$$

$$\Delta_{\text{expt}}(^2P_{3/2} \rightarrow ^4S_{3/2}) = 4.11 \text{ eV}$$