JÜLICH
FORSCHUNGSZENTRUM

Calculations of atomic multiplets across the periodic table

Master's Thesis

14 October 2014 | Qian Zhang Prof. Dr. Erik Koch |

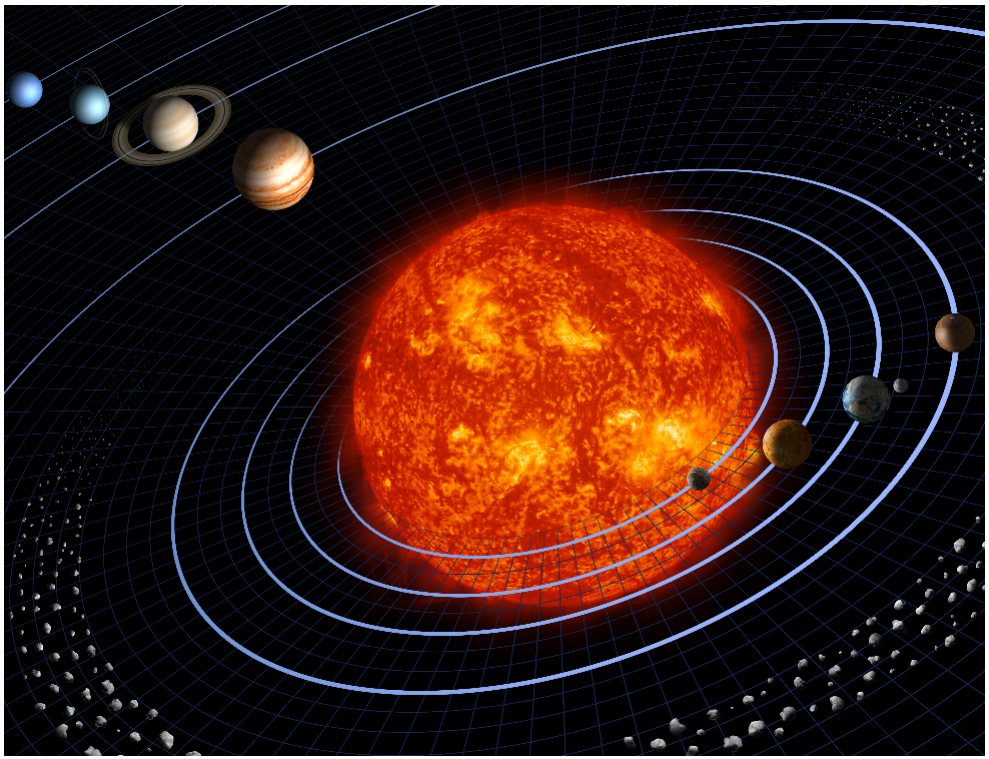
German Research School for Simulation Sciences RWTH Aachen University

Outline

1. Introduction
2. The one-electron problem
3. The many-electron problem (mean-field approximation)
4. Construction of multiplet states
5. Spin-orbit coupling
6. Conclusion

Introduction

Imagine our solar system...



(Image from NASA)

$$\mathbf{F} = m\mathbf{a}$$

Mercury: $\mathbf{r}_1(t)$

Venus: $\mathbf{r}_2(t)$

Earth: $\mathbf{r}_3(t)$

Mars: $\mathbf{r}_4(t)$

$\vdots$

Introduction

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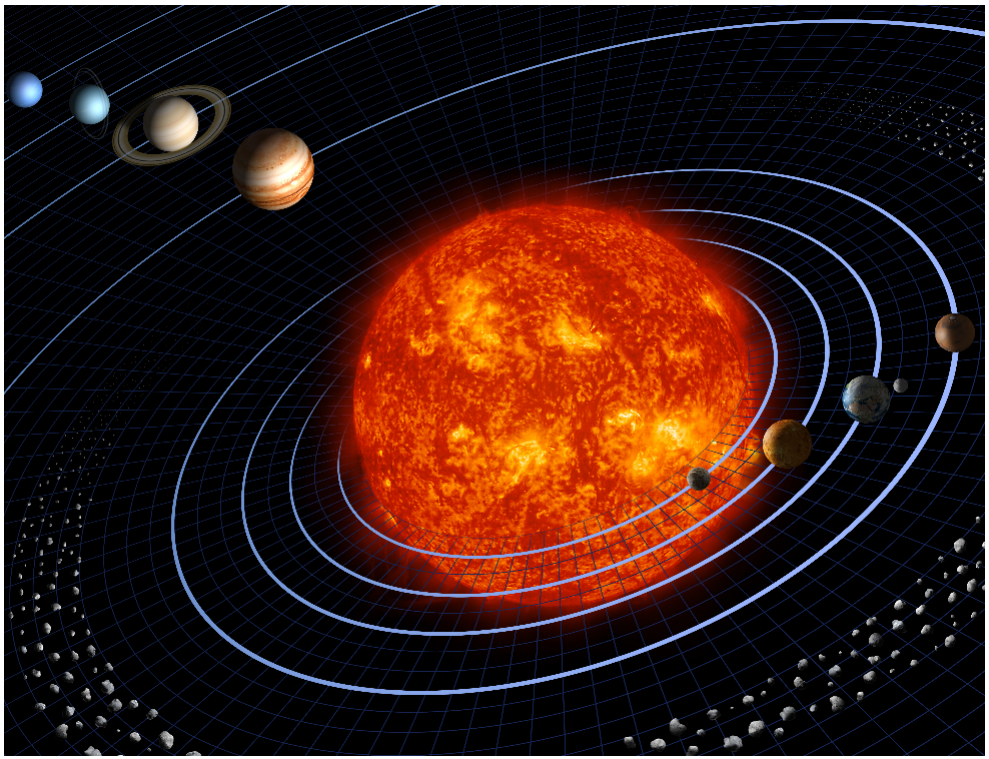

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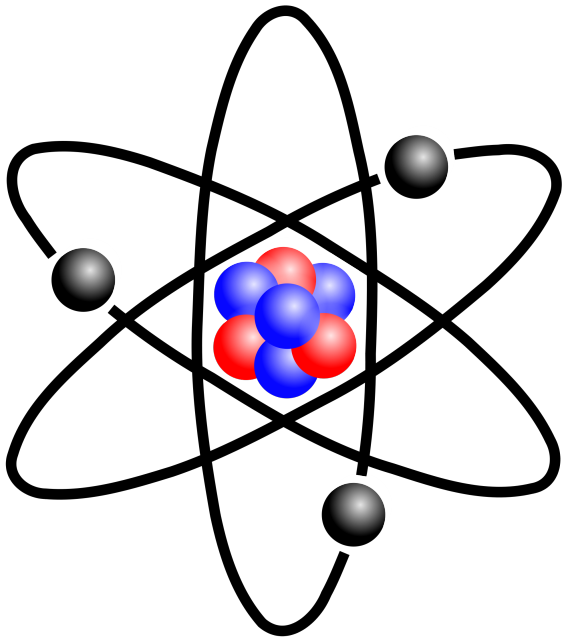
$\vdots$

Analytical solution: ✗
Numerical solution: ✓

Introduction

Scaling down to 10^{-10} meters...



(Image from Wikipedia)

$$H\Psi = E\Psi$$

$$H = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Many-electron wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

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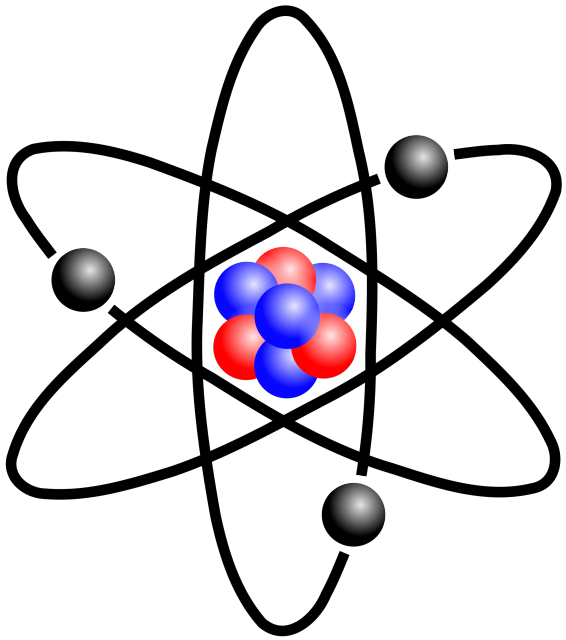

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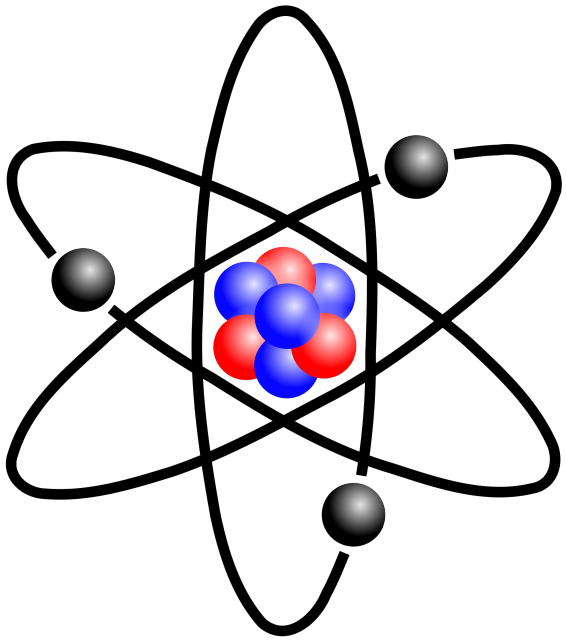

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Analytical solution: ✗
Numerical solution: ✗

Approximations!

One-electron problem

For $N = 1$

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\varphi = E\varphi$$

Separation of variables:

$$\varphi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$$

Angular part	$Y(\theta,\phi)$	Easy, spherical harmonics
Radial part	$R(r)$	Difficult, our task

One-electron problem

Angular equation

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}=-l(l+1)Y$$

One-electron problem

Angular equation

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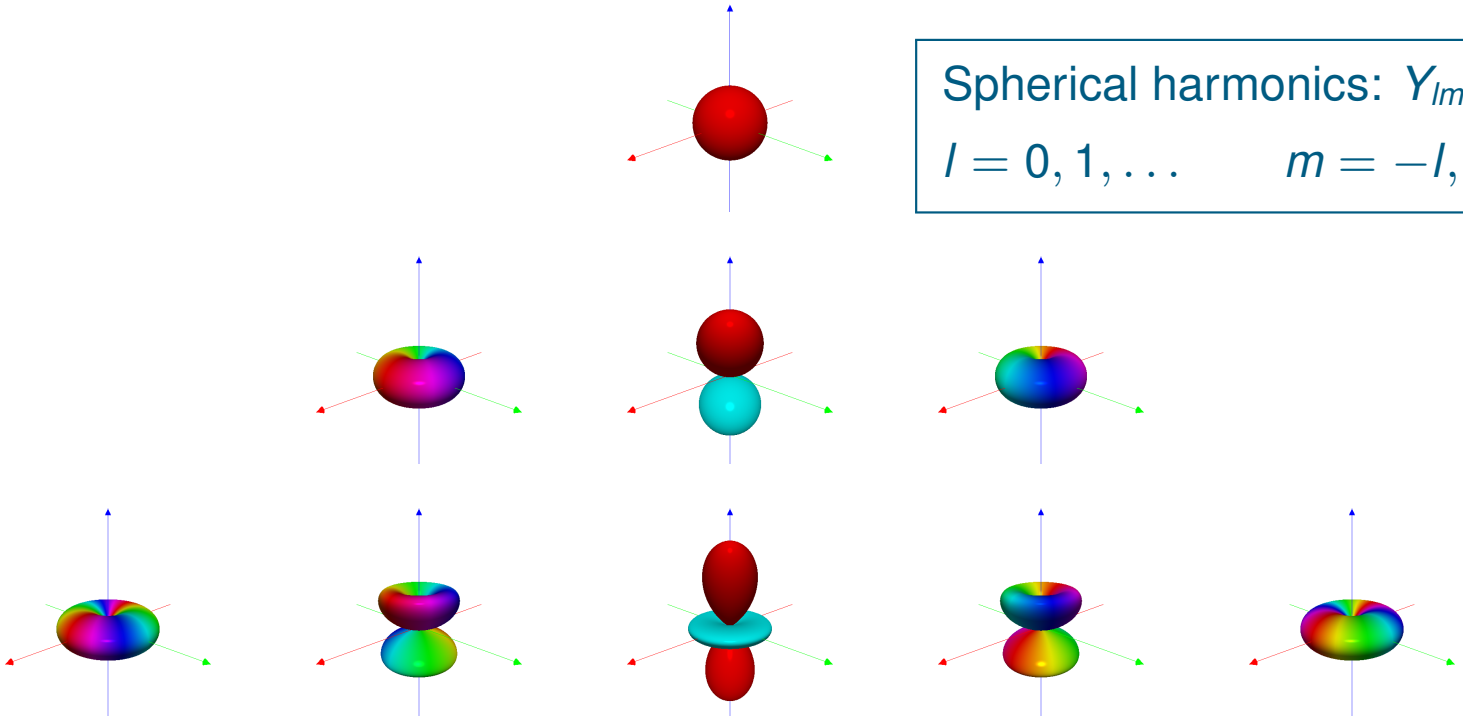

Spherical harmonics: $Y_{lm}(\theta,\phi)$

$l=0,1,\ldots \qquad m=-l,\ldots,l$

One-electron problem

Define $u(r) \equiv rR(r)$, radial equation

$$\boxed{-\frac{1}{2}\frac{d^2u}{dr^2} + \left[V(r) + \frac{l(l+1)}{2r^2}\right] u = Eu}$$

where $V(r) = -Z/r$

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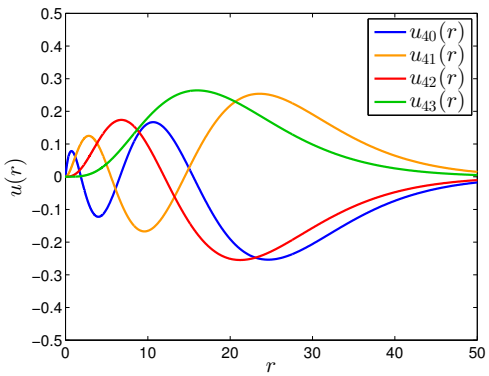
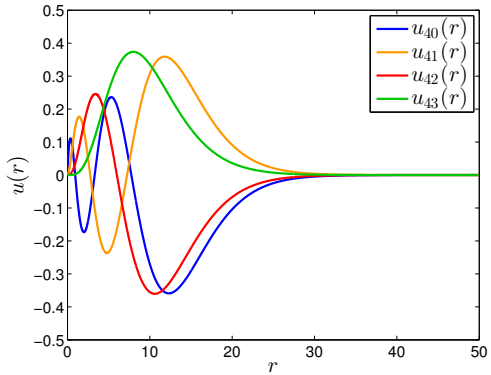
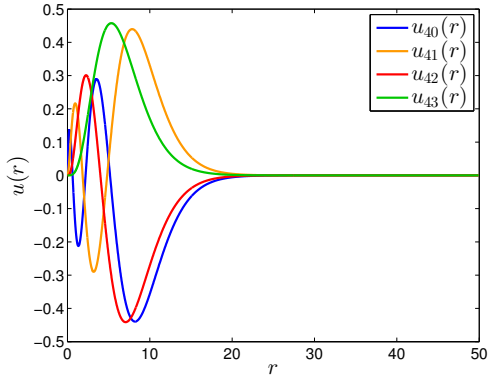


(a) $Z = 1$



(b) $Z = 2$

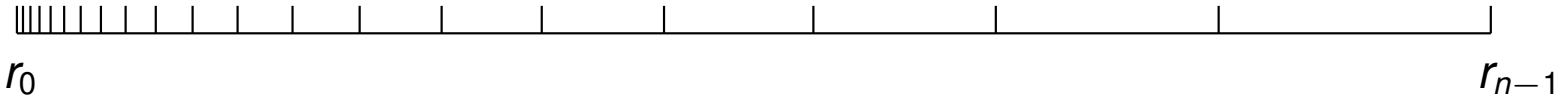


(c) $Z = 3$

Logarithmic grid

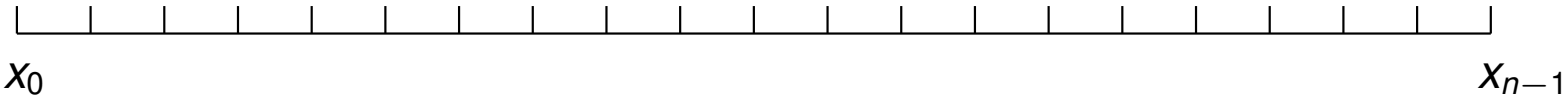
Construct a logarithmic grid, $0 < r_0 < \cdots < r_{n-1} < \infty$, where

$$r_i = \frac{1}{Z} e^{x_i}$$



and x is a uniformly distributed grid

$$x_i = x_0 + i\Delta x$$



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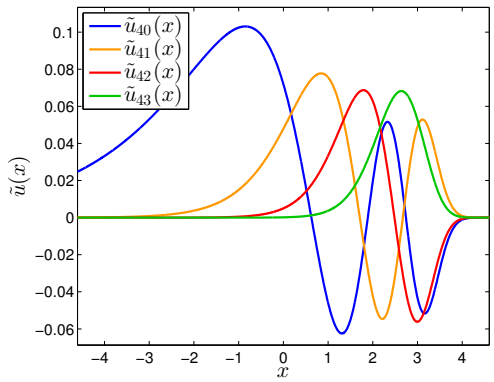

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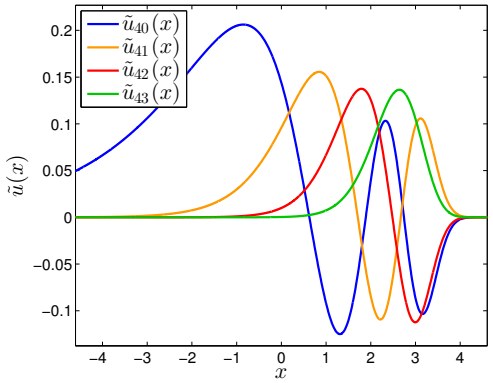
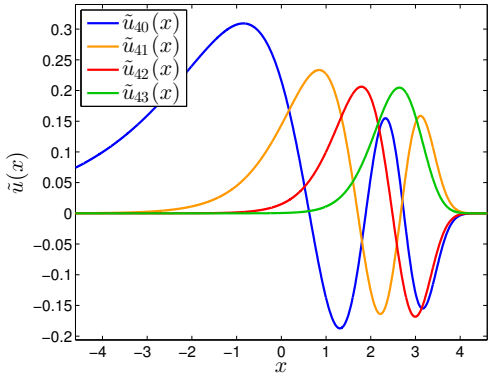


(b) $Z = 2$



(c) $Z = 3$

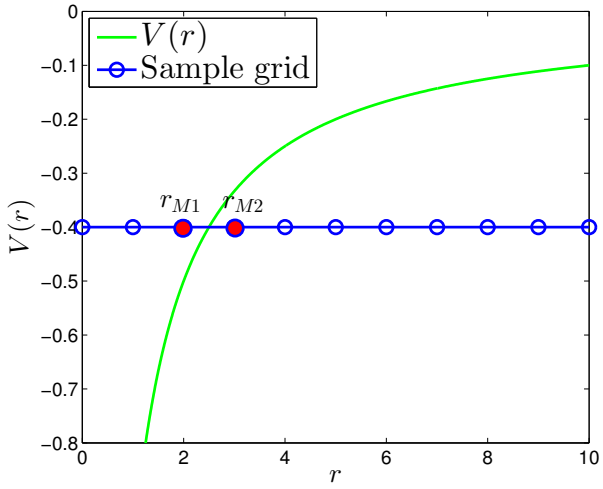
Rescale $\tilde{u} \equiv u/\sqrt{r}$, the transformed radial equation

$$-\frac{1}{2}\frac{d^2\tilde{u}}{dx^2} + \left[r^2 V(r) + \frac{1}{2}\left(l + \frac{1}{2}\right)^2\right]\tilde{u} = r^2 E\tilde{u}$$

The shooting and matching methods

Numerov's method

$$\tilde{u}_{i\pm1} = \frac{(2 - \frac{5\Delta x^2}{3} k_i^2)\tilde{u}_i - (1 + \frac{\Delta x^2}{6} k_{i\mp1}^2)\tilde{u}_{i\mp1}}{1 + \frac{\Delta x^2}{6} k_{i\pm1}^2}$$



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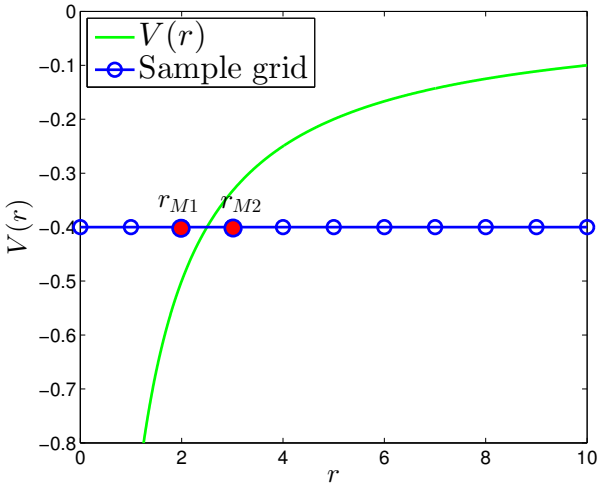

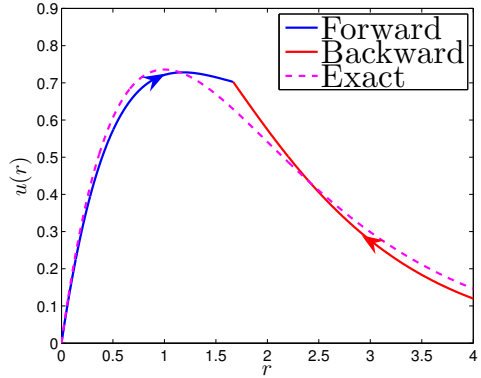

(a) $E = -0.6$

The shooting and matching methods

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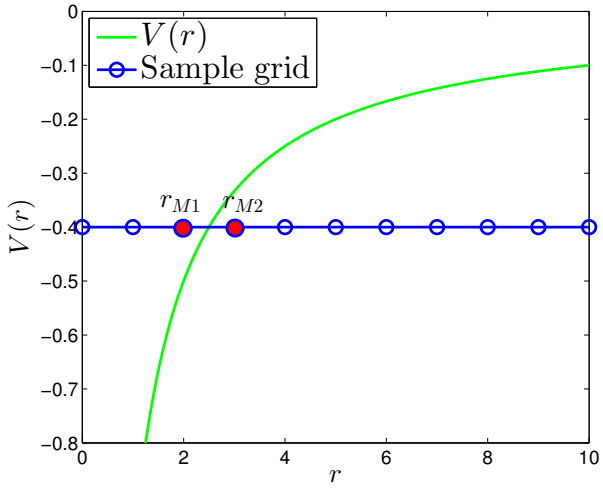

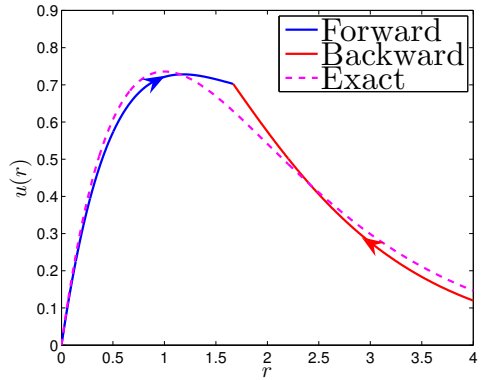

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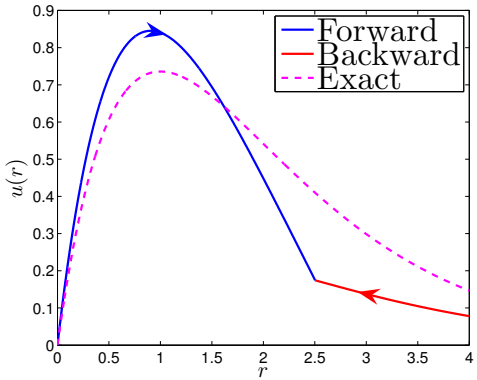
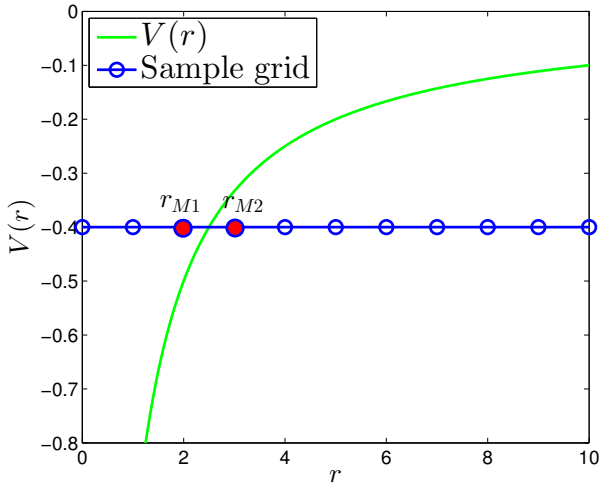


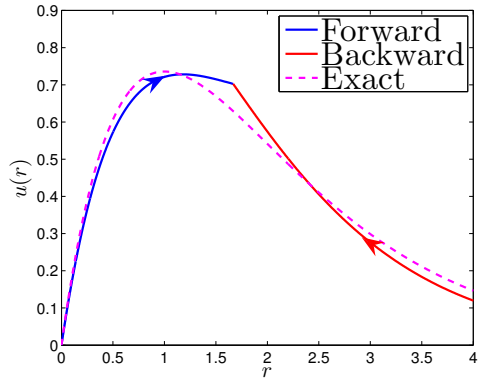
(b) $E = -0.4$

The shooting and matching methods

Numerov's method

$$\tilde{u}_{i\pm1} = \frac{(2 - \frac{5\Delta x^2}{3} k_i^2)\tilde{u}_i - (1 + \frac{\Delta x^2}{6} k_{i\mp1}^2)\tilde{u}_{i\mp1}}{1 + \frac{\Delta x^2}{6} k_{i\pm1}^2}$$





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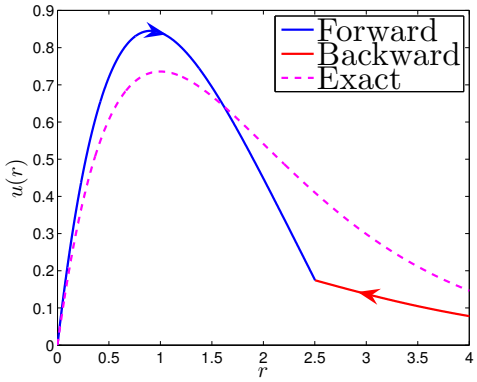
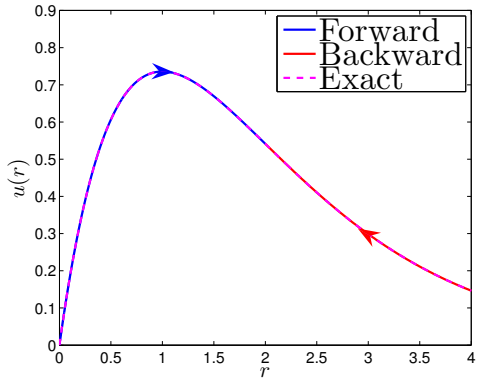


(b) $E = -0.4$



(c) $E = -0.5$

Numerical and exact eigen-energy comparison

Elem	Orbital	Numerical	Exact	Abs Error	Rel Error
H	1*s*	−0.500000	−0.500000	0.000000	0.000000
C	1*s*	−18.000002	−18.000000	0.000002	0.000000
	2*s*	−4.499999	−4.500000	0.000001	0.000000
	2*p*	−4.500001	−4.500000	0.000001	0.000000
Fe	1*s*	−338.000032	−338.000000	0.000032	0.000000
	2*s*	−84.499984	−84.500000	0.000016	0.000000
	2*p*	−84.500012	−84.500000	0.000012	0.000000
	3*s*	−37.555556	−37.555556	0.000000	0.000000
	3*p*	−37.555556	−37.555556	0.000000	0.000000
	3*d*	−37.555555	−37.555556	0.000001	0.000000
	4*s*	−21.125000	−21.125000	0.000000	0.000000

One electron only!

The many-electron problem

Many-electron Schrödinger equation

$$\left\{ \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right\} \Psi = E\Psi$$

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- Analytical solution: ✗
- Numerical solution: ✗
- We use self-consistent field (SCF) approximation

The many-electron problem

Hartree ansatz

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \approx \varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\ldots\varphi_N(\mathbf{r}_N)$$

Mean-field approximation

$$H = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right] + \underbrace{\sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{Trouble maker}}$$

$$H = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right] + \underbrace{V_{\text{Hartree}}(r)}_{\text{Hartree potential}}$$

Self-consistent iteration

Many-electron problem $\rightarrow$ Many one-electron problems

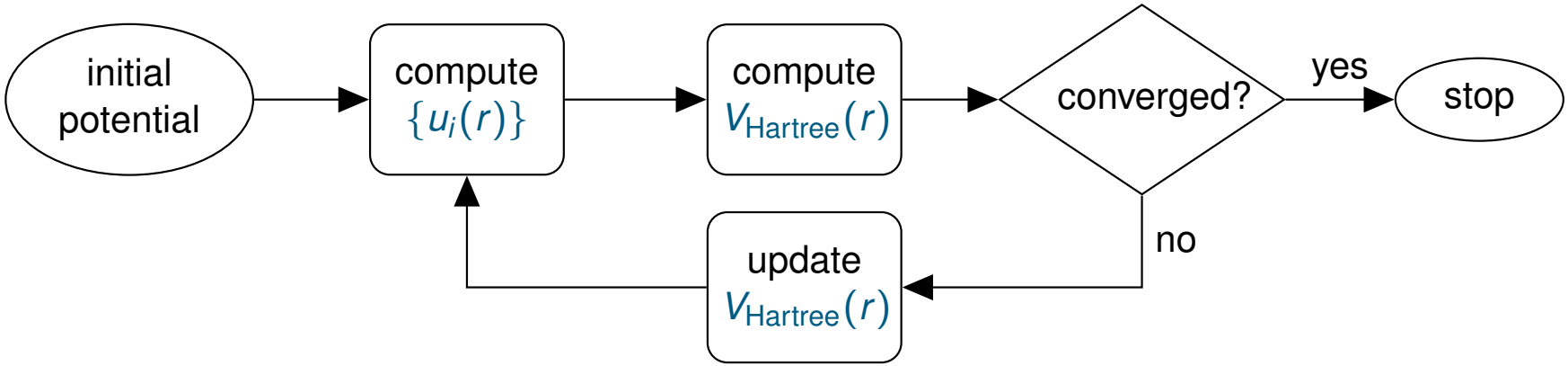
$$\boxed{-\frac{1}{2}\frac{d^2 u_i}{dr^2} + \left[V_{\text{ext}}(r) + V_{\text{Hartree}}(r) + \frac{l(l+1)}{2r^2}\right] u_i = E_i u_i}$$

Self-consistent iteration

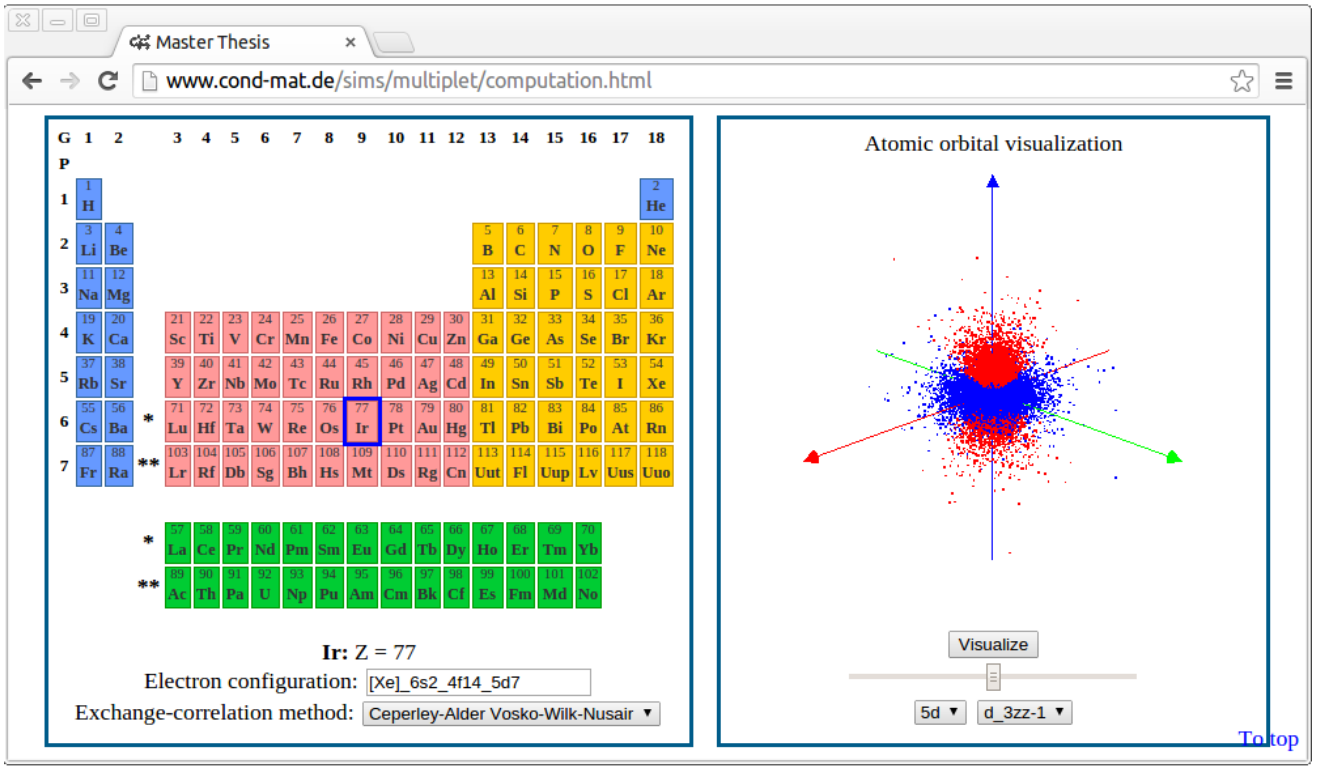
Many-electron problem $\rightarrow$ Many one-electron problems

$$-\frac{1}{2}\frac{d^2 u_i}{dr^2} + \left[V_{\text{ext}}(r) + V_{\text{Hartree}}(r) + \frac{l(l+1)}{2r^2}\right] u_i = E_i u_i$$

Chicken or the egg problem!



JavaScript demonstration



www.cond-mat.de/sims/multiplet

Comparison to NIST results

Elem	Orbital	My results	NIST results	Abs Error	Rel Error
H	$1s^1$	−0.233471	−0.233471	0.000000	0.000000
C	$1s^2$	−9.947725	−9.947718	0.000007	0.000001
	$2s^2$	−0.500866	−0.500866	0.000000	0.000000
	$2p^2$	−0.199186	−0.199186	0.000000	0.000000
Fe	$1s^2$	−254.225334	−254.225505	0.000171	0.000001
	$2s^2$	−29.564863	−29.564860	0.000003	0.000000
	$2p^6$	−25.551762	−25.551766	0.000004	0.000000
	$3s^2$	−3.360622	−3.360621	0.000001	0.000000
	$3p^6$	−2.187521	−2.187523	0.000002	0.000001
	$3d^6$	−0.295047	−0.295049	0.000002	0.000007
	$4s^2$	−0.197976	−0.197978	0.000002	0.000010

Many-electron, mean-field!

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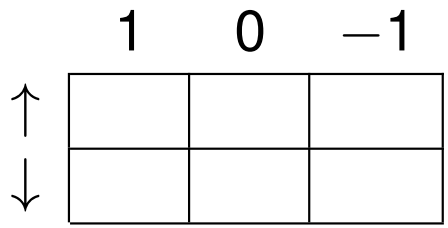
Many-electron, mean-field!

Open shell problem

Imagine the following problem:

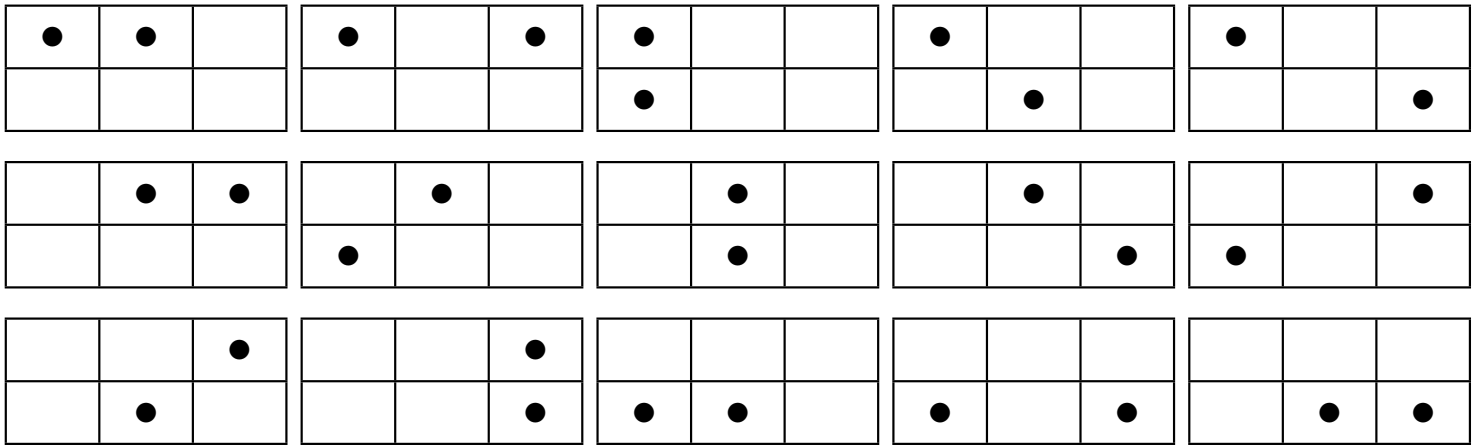


and

p shell

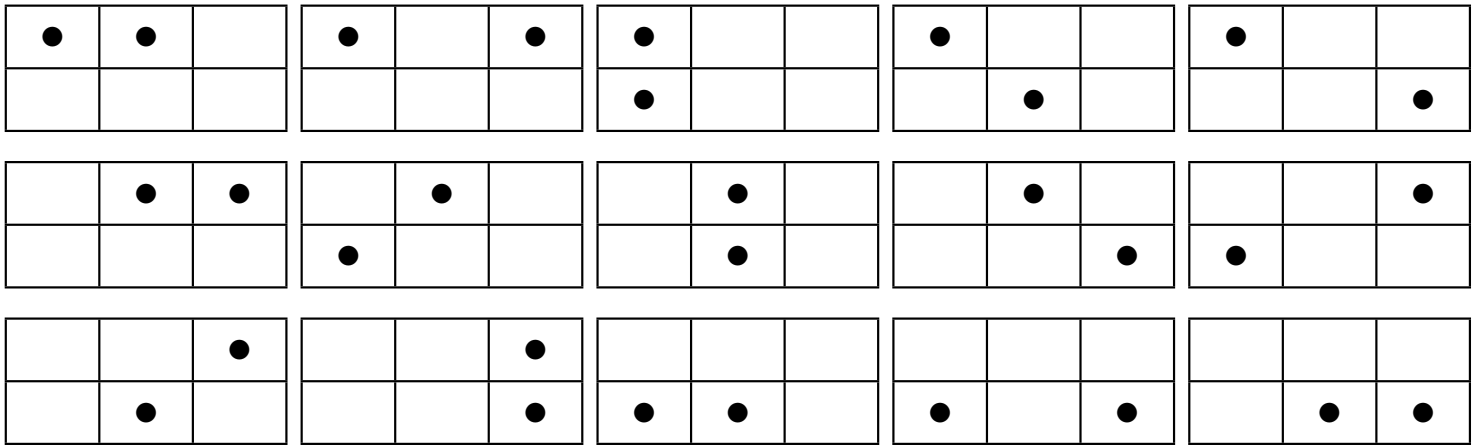
2 electrons

Open shell problem



Which configuration has the highest energy?

Open shell problem



Which configuration has the highest energy?

$$\frac{1}{\sqrt{3}}\;\square\!\bullet\!\square\!\bullet\;-\;\frac{1}{\sqrt{3}}\;\square\!\bullet\!\bullet\!\square\;+\;\frac{1}{\sqrt{3}}\;\bullet\!\square\!\square\!\bullet$$

Coulomb repulsion Hamiltonian

Revisit our trouble maker

$$H_U = \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Second quantization

$$H_U = \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha\beta\gamma\delta} c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta$$

$$\alpha = \{n_1, l_1, m_1, \sigma_1\}$$
$$\beta = \{n_2, l_2, m_2, \sigma_2\}$$
$$\gamma = \{n_3, l_3, m_3, \sigma_3\}$$
$$\delta = \{n_4, l_4, m_4, \sigma_4\}$$

Coulomb repulsion Hamiltonian

Coulomb repulsion matrix element

$$U_{\alpha\beta\gamma\delta} =$$

$$\delta_{\sigma_1\sigma_4}\delta_{\sigma_2\sigma_3}\int d^3r_1 \int d^3r_2\, \overline{\varphi_{n_1 l_1 m_1}}(\mathbf{r}_1)\overline{\varphi_{n_2 l_2 m_2}}(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\varphi_{n_3 l_3 m_3}(\mathbf{r}_2)\varphi_{n_4 l_4 m_4}(\mathbf{r}_1)$$

Coulomb repulsion Hamiltonian

Coulomb repulsion matrix element

$$U_{\alpha\beta\gamma\delta} =$$

$$\delta_{\sigma_1\sigma_4}\delta_{\sigma_2\sigma_3}\int d^3r_1 \int d^3r_2\, \overline{\varphi_{n_1 l_1 m_1}}(\mathbf{r}_1)\overline{\varphi_{n_2 l_2 m_2}}(\mathbf{r}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\varphi_{n_3 l_3 m_3}(\mathbf{r}_2)\varphi_{n_4 l_4 m_4}(\mathbf{r}_1)$$

Multipole expansion

$$\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} = \sum_{k=0}^{\infty} \underbrace{\frac{r_<^k}{r_>^{k+1}}}_{\text{Radial part}} \frac{4\pi}{2k+1} \sum_{\mu=-k}^{k} \underbrace{\overline{Y_{k\mu}}(\theta_1,\phi_1)Y_{k\mu}(\theta_2,\phi_2)}_{\text{Angular part}}$$

Coulomb repulsion Hamiltonian

The radial part

$$R^{(k)}(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) = \int_0^\infty dr_1 \int_0^\infty dr_2 \, \overline{u_{n_1 l_1}}(r_1) \overline{u_{n_2 l_2}}(r_2) \frac{r_<^k}{r_>^{k+1}} u_{n_3 l_3}(r_2) u_{n_4 l_4}(r_1)$$

The angular part

$$A^{(k)}(l_1 m_1, l_2 m_2, l_3 m_3, l_4 m_4) =$$

$$\sum_{\mu=-k}^{k} \int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \, \sin\theta_1 \, \overline{Y_{l_1 m_1}}(\theta_1, \phi_1) \overline{Y_{k\mu}}(\theta_1, \phi_1) Y_{l_4 m_4}(\theta_1, \phi_1)$$

$$\int_0^{2\pi} d\phi_2 \int_0^{\pi} d\theta_2 \, \sin\theta_2 \, \overline{Y_{l_2 m_2}}(\theta_2, \phi_2) Y_{k\mu}(\theta_2, \phi_2) Y_{l_3 m_3}(\theta_2, \phi_2)$$

Coulomb repulsion Hamiltonian

The radial part

$$R^{(k)}(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) = \int_0^\infty dr_1 \int_0^\infty dr_2 \, \overline{u_{n_1 l_1}}(r_1) \overline{u_{n_2 l_2}}(r_2) \frac{r_<^k}{r_>^{k+1}} u_{n_3 l_3}(r_2) u_{n_4 l_4}(r_1)$$

The angular part

Slater-Condon parameters

$$A^{(k)}(l_1 m_1, l_2 m_2, l_3 m_3, l_4 m_4) =$$

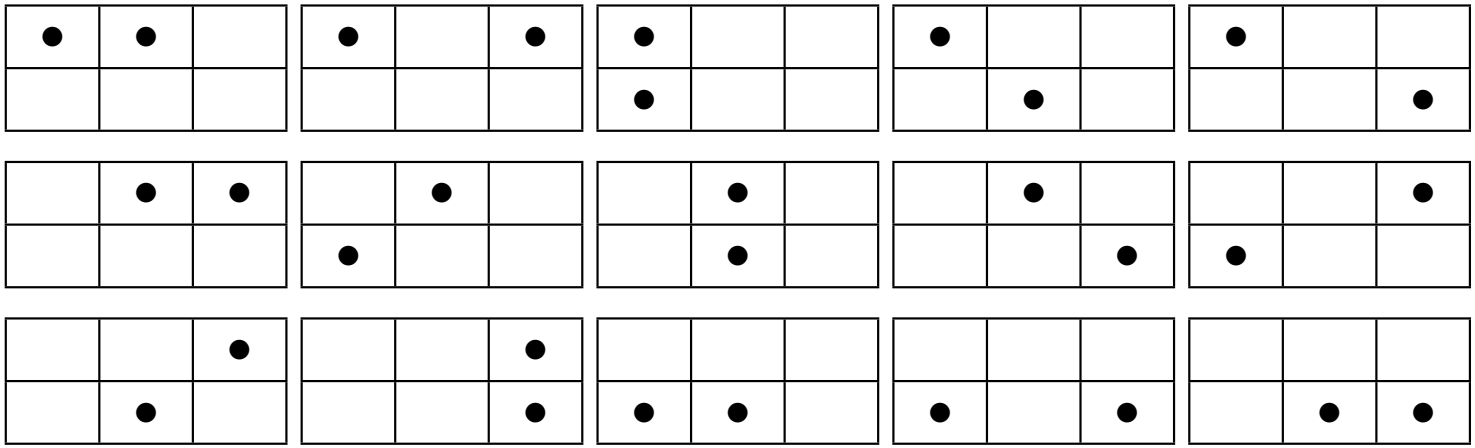
$$\sum_{\mu=-k}^{k} \int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \, \sin\theta_1 \, \overline{Y_{l_1 m_1}}(\theta_1, \phi_1) \overline{Y_{k\mu}}(\theta_1, \phi_1) Y_{l_4 m_4}(\theta_1, \phi_1)$$

$$\int_0^{2\pi} d\phi_2 \int_0^{\pi} d\theta_2 \, \sin\theta_2 \, \overline{Y_{l_2 m_2}}(\theta_2, \phi_2) Y_{k\mu}(\theta_2, \phi_2) Y_{l_3 m_3}(\theta_2, \phi_2)$$

Gaunt coefficients

Setting up basis and Hamiltonian

Set up basis



$|110000\rangle$ $|101000\rangle$ $|100100\rangle$ $|100010\rangle$ $|100001\rangle$
$|011000\rangle$ $|010100\rangle$ $|010010\rangle$ $|010001\rangle$ $|001100\rangle$
$|001010\rangle$ $|001001\rangle$ $|000110\rangle$ $|000101\rangle$ $|000011\rangle$

Setting up basis and Hamiltonian

Set up Hamiltonian

$$\langle i| H_U |j\rangle = \langle i| \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha\beta\gamma\delta} c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta |j\rangle$$

$$H_U = \begin{bmatrix} \otimes & & & & & & & & & & & & & & & & & & & & \\ & \otimes & & & & & & & & & & & & & & & & & & \\ & & \otimes & & & & & & & & & & & & & & & & & \\ & & & \otimes & & & & & & & & & & & & & & & & \\ & & & & \otimes & & \otimes & & & & & & & & & & & & & \\ & & & & & \otimes & & \otimes & & & \otimes & & & & & & & & & \\ & & & & \otimes & & \otimes & & & & & & & & & & & & & \\ & & & & & \otimes & & \otimes & & & \otimes & & & & & & & & & \\ & & & & & & & & \otimes & & & \otimes & & & & & & & & \\ & & & & & & & & & \otimes & & & & & & & & & & \\ & & & & & \otimes & & \otimes & & & \otimes & & & & & & & & & \\ & & & & & & & & \otimes & & & \otimes & & & & & & & & \\ & & & & & & & & & & & & \otimes & & & & & & & \\ & & & & & & & & & & & & & \otimes & & & & & & \\ & & & & & & & & & & & & & & \otimes & & & & & \end{bmatrix} \begin{matrix} |000011\rangle \\ |000101\rangle \\ |000110\rangle \\ |001001\rangle \\ |001010\rangle \\ |001100\rangle \\ |010001\rangle \\ |010010\rangle \\ |010100\rangle \\ |011000\rangle \\ |100001\rangle \\ |100010\rangle \\ |100100\rangle \\ |101000\rangle \\ |110000\rangle \end{matrix}$$

Setting up basis and Hamiltonian

Set up Hamiltonian

$$\langle i|\, H_U \,|j\rangle = \langle i|\, \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha\beta\gamma\delta} c^\dagger_\alpha c^\dagger_\beta c_\gamma c_\delta \,|j\rangle$$

$$H_U = \begin{bmatrix}
\otimes & & & & & & & & & & & & & & \\
 & \otimes & & & & & & & & & & & & & \\
 & & \otimes & \otimes & & & & & & & & & & & \\
 & & \otimes & \otimes & & & & & & & & & & & \\
 & & & & \otimes & & & & & & & & & & \\
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 & & & & & & & & & & & \otimes & \otimes & & \\
 & & & & & & & & & & & \otimes & \otimes & & \\
 & & & & & & & & & & & & & \otimes & \\
 & & & & & & & & & & & & & & \otimes
\end{bmatrix}$$

	$\lvert M_L\ M_S\rangle$
$\lvert 100100\rangle$	$\lvert\ 2\ \ 0\rangle$
$\lvert 110000\rangle$	$\lvert\ 1\ \ 1\rangle$
$\lvert 010100\rangle$	$\lvert\ 1\ \ 0\rangle$
$\lvert 100010\rangle$	$\lvert\ 1\ \ 0\rangle$
$\lvert 000110\rangle$	$\lvert\ 1\ -1\rangle$
$\lvert 101000\rangle$	$\lvert\ 0\ \ 1\rangle$
$\lvert 001100\rangle$	$\lvert\ 0\ \ 0\rangle$
$\lvert 010010\rangle$	$\lvert\ 0\ \ 0\rangle$
$\lvert 100001\rangle$	$\lvert\ 0\ \ 0\rangle$
$\lvert 000101\rangle$	$\lvert\ 0\ -1\rangle$
$\lvert 011000\rangle$	$\lvert -1\ \ 1\rangle$
$\lvert 001010\rangle$	$\lvert -1\ \ 0\rangle$
$\lvert 010001\rangle$	$\lvert -1\ \ 0\rangle$
$\lvert 000011\rangle$	$\lvert -1\ -1\rangle$
$\lvert 001001\rangle$	$\lvert -2\ \ 0\rangle$

Construction of multiplet states

Commutation relations

$$[H_U, \mathbf{L}] = 0 \qquad [H_U, \mathbf{S}] = 0$$

$$[H_U, L^2] = 0 \qquad [H_U, L_z] = 0 \qquad [H_U, S^2] = 0 \qquad [H_U, S_z] = 0$$

We can represent an eigen-vector

$$|L, M_L, S, M_S\rangle$$

Construction of multiplet states

Commutation relations

$$[H_U, \mathbf{L}] = 0 \qquad [H_U, \mathbf{S}] = 0$$

$$[H_U, L^2] = 0 \qquad [H_U, L_z] = 0 \qquad [H_U, S^2] = 0 \qquad [H_U, S_z] = 0$$

We can represent an eigen-vector

$$|L, M_L, S, M_S\rangle$$

Commutation relations

$$[H_U, L_\pm] = 0 \qquad [H_U, S_\pm] = 0$$

Starting from a leading vector, we can construct subsequent vectors by applying ladder operators.

Construction of multiplet states

M_L-M_S table

		M_S		
		-1	0	1
	2	0	1	0
	1	1	2	1
M_L	0	1	3	1
	-1	1	2	1
	-2	0	1	0

$$|1, \quad 1, 1, \quad 1\rangle$$

Construction of multiplet states

M_L-M_S table

		M_S		
		-1	0	1
	2	0	1	0
	1	1	2	1
M_L	0	1	3	1
	-1	1	2	1
	-2	0	1	0

$$
\begin{array}{lll}
|1,\ \ 1,1,-1\rangle & |1,\ \ 1,1,\ \ 0\rangle & |1,\ \ 1,1,\ \ 1\rangle \\
|1,\ \ 0,1,-1\rangle & |1,\ \ 0,1,\ \ 0\rangle & |1,\ \ 0,1,\ \ 1\rangle \\
|1,-1,1,-1\rangle & |1,-1,1,\ \ 0\rangle & |1,-1,1,\ \ 1\rangle
\end{array}
$$

^3P

Construction of multiplet states

M_L-M_S table

		M_S		
		-1	0	1
	2	0	**1**	0
	1	0	1	0
M_L	0	0	2	0
	-1	0	1	0
	-2	0	1	0

$$|2, \quad 2, 0, \quad 0\rangle$$

Construction of multiplet states

M_L-M_S table

		M_S		
		-1	0	1
	2	0	**1**	0
	1	0	**1**	0
M_L	0	0	**2**	0
	-1	0	**1**	0
	-2	0	**1**	0

$$
\begin{aligned}
&|2, \quad 2, 0, \quad 0\rangle \\
&|2, \quad 1, 0, \quad 0\rangle \\
&|2, \quad 0, 0, \quad 0\rangle \\
&|2, -1, 0, \quad 0\rangle \\
&|2, -2, 0, \quad 0\rangle
\end{aligned}
$$

^1D

Construction of multiplet states

M_L-M_S table

		M_S		
		-1	0	1
	2	0	0	0
	1	0	0	0
M_L	0	0	**1**	0
	-1	0	0	0
	-2	0	0	0

$$|0, \quad 0, 0, \quad 0\rangle$$

^1S

Construction of multiplet states

Three groups of eigen-vectors

^3P			^1D	^1S
			$\|2, 2, 0, 0\rangle$	
$\|1, 1, 1, -1\rangle$	$\|1, 1, 1, 0\rangle$	$\|1, 1, 1, 1\rangle$	$\|2, 1, 0, 0\rangle$	
$\|1, 0, 1, -1\rangle$	$\|1, 0, 1, 0\rangle$	$\|1, 0, 1, 1\rangle$	$\|2, 0, 0, 0\rangle$	$\|0, 0, 0, 0\rangle$
$\|1, -1, 1, -1\rangle$	$\|1, -1, 1, 0\rangle$	$\|1, -1, 1, 1\rangle$	$\|2, -1, 0, 0\rangle$	
			$\|2, -2, 0, 0\rangle$	

Multiplet term symbol

$$^{2S+1}L$$

Construction of multiplet states

In summary, our 15 eigen-vectors:

^3P	$\lvert 1, \quad 1, 1, \quad 1\rangle$	$=$	$c^\dagger_{0\uparrow} c^\dagger_{1\uparrow} \lvert 0\rangle$
	$\lvert 1, \quad 1, 1, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(-c^\dagger_{1\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{0\downarrow} c^\dagger_{1\uparrow} \right) \lvert 0\rangle$
	$\lvert 1, \quad 1, 1, -1\rangle$	$=$	$c^\dagger_{0\downarrow} c^\dagger_{1\downarrow} \lvert 0\rangle$
	$\lvert 1, \quad 0, 1, \quad 1\rangle$	$=$	$c^\dagger_{-1\uparrow} c^\dagger_{1\uparrow} \lvert 0\rangle$
	$\lvert 1, \quad 0, 1, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(-c^\dagger_{1\downarrow} c^\dagger_{-1\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{1\uparrow} \right) \lvert 0\rangle$
	$\lvert 1, \quad 0, 1, -1\rangle$	$=$	$c^\dagger_{-1\downarrow} c^\dagger_{1\downarrow} \lvert 0\rangle$
	$\lvert 1, -1, 1, \quad 1\rangle$	$=$	$c^\dagger_{-1\uparrow} c^\dagger_{0\uparrow} \lvert 0\rangle$
	$\lvert 1, -1, 1, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(-c^\dagger_{0\downarrow} c^\dagger_{-1\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{0\uparrow} \right) \lvert 0\rangle$
	$\lvert 1, -1, 1, -1\rangle$	$=$	$c^\dagger_{-1\downarrow} c^\dagger_{0\downarrow} \lvert 0\rangle$

Construction of multiplet states

In summary, our 15 eigen-vectors:

^1D	$\|2, 2, 0, 0\rangle$	$=$	$c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} \|0\rangle$
	$\|2, 1, 0, 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(c^\dagger_{1\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{0\downarrow} c^\dagger_{1\uparrow} \right) \|0\rangle$
	$\|2, 0, 0, 0\rangle$	$=$	$\frac{1}{\sqrt{6}} \left(c^\dagger_{1\downarrow} c^\dagger_{-1\uparrow} + 2 c^\dagger_{0\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{1\uparrow} \right) \|0\rangle$
	$\|2, -1, 0, 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(c^\dagger_{0\downarrow} c^\dagger_{-1\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{0\uparrow} \right) \|0\rangle$
	$\|2, -2, 0, 0\rangle$	$=$	$c^\dagger_{-1\downarrow} c^\dagger_{-1\uparrow} \|0\rangle$
^1S	$\|0, 0, 0, 0\rangle$	$=$	$\frac{1}{\sqrt{3}} \left(c^\dagger_{1\downarrow} c^\dagger_{-1\uparrow} - c^\dagger_{0\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{1\uparrow} \right) \|0\rangle$

Construction of multiplet states

In summary, our 15 eigen-vectors:

${}^1D$	$\lvert 2, \quad 2, 0, \quad 0\rangle$	$=$	$c^\dagger_{1\downarrow} c^\dagger_{1\uparrow} \lvert 0\rangle$
	$\lvert 2, \quad 1, 0, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(c^\dagger_{1\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{0\downarrow} c^\dagger_{1\uparrow} \right) \lvert 0\rangle$
	$\lvert 2, \quad 0, 0, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{6}} \left(c^\dagger_{1\downarrow} c^\dagger_{-1\uparrow} + 2 c^\dagger_{0\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{1\uparrow} \right) \lvert 0\rangle$
	$\lvert 2, -1, 0, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{2}} \left(c^\dagger_{0\downarrow} c^\dagger_{-1\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{0\uparrow} \right) \lvert 0\rangle$
	$\lvert 2, -2, 0, \quad 0\rangle$	$=$	$c^\dagger_{-1\downarrow} c^\dagger_{-1\uparrow} \lvert 0\rangle$
${}^1S$	$\lvert 0, \quad 0, 0, \quad 0\rangle$	$=$	$\frac{1}{\sqrt{3}} \left(c^\dagger_{1\downarrow} c^\dagger_{-1\uparrow} - c^\dagger_{0\downarrow} c^\dagger_{0\uparrow} + c^\dagger_{-1\downarrow} c^\dagger_{1\uparrow} \right) \lvert 0\rangle$

Eigen-energy of multiplet states

Eigen-vector

$$|\mathbf{v}_n\rangle$$

Eigen-energy of multiplet states

Eigen-vector

$$|\mathbf{v}_n\rangle$$

Eigen-energy

$$E_n = \langle \mathbf{v}_n | \, H_U \, | \mathbf{v}_n \rangle$$

Eigen-energy of multiplet states

Eigen-vector

$$|\mathbf{v}_n\rangle$$

Eigen-energy

$$E_n = \langle \mathbf{v}_n | \, H_U \, | \mathbf{v}_n \rangle$$

Carbon atom p^2 orbital

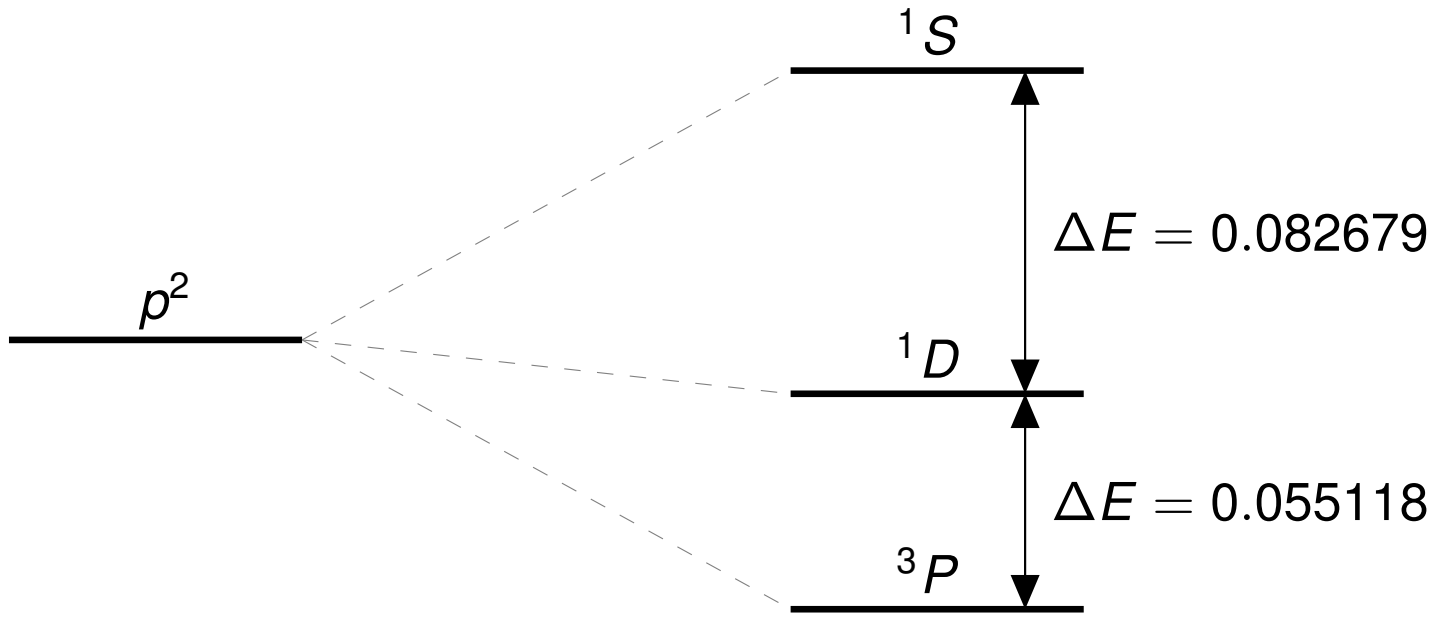
$$^1S : 0.612081 \text{ (Hartree)}$$

$$^1D : 0.529402 \text{ (Hartree)}$$

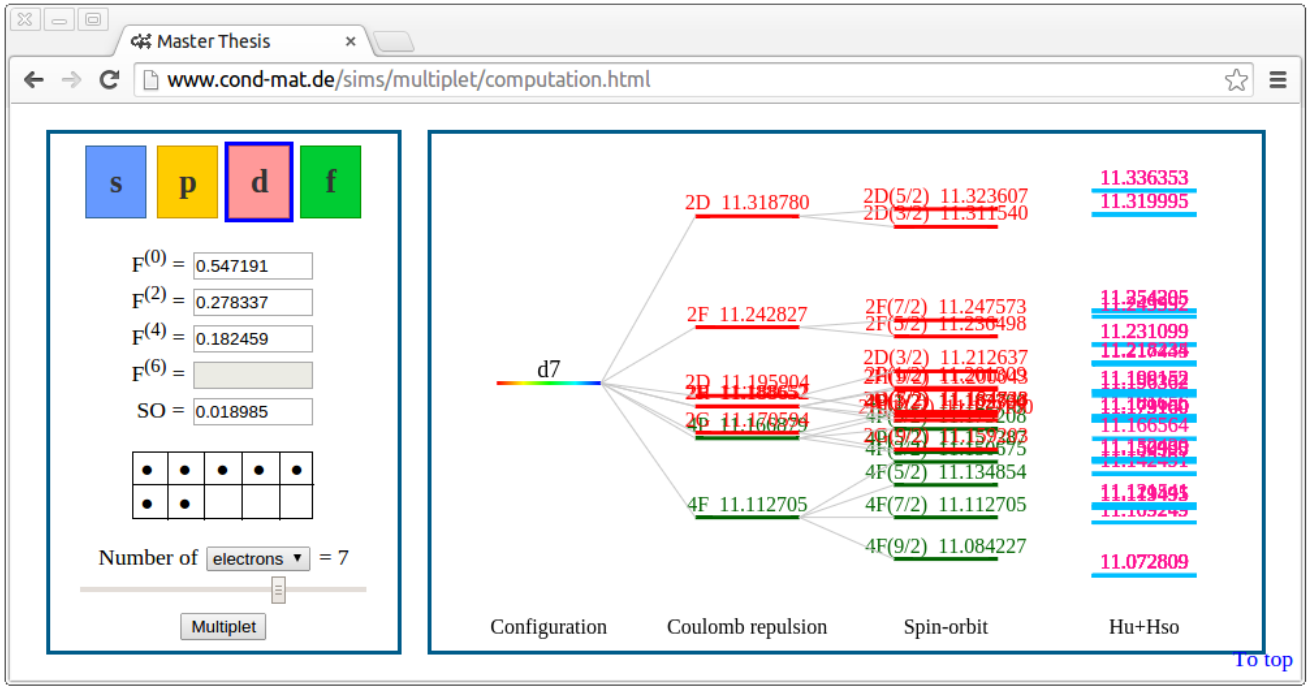
$$^3P : 0.474284 \text{ (Hartree)}$$

Eigen-energy of multiplet states

Energy splitting



JavaScript demonstration



www.cond-mat.de/sims/multiplet

Spin-orbit coupling

Our original Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Spin-orbit coupling

Our original Hamiltonian

$$H = \sum_{i=1}^{N} \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right] + \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

A magnetic force?

Spin-orbit coupling

The Hamiltonian with spin-orbit effect

$$H = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right] + \sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \underbrace{\sum_{i=1}^{N}\xi(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i}_{\text{Weak}}$$

where,

$$\xi(r) = \frac{1}{2c^2}\frac{1}{r}\frac{dV}{dr}$$

In atomic units

$$c \approx 137.036\ \mathrm{a_0/t_0}$$

Spin-orbit coupling within multiplet terms

Clebsch-Grodan transformation

$$|L, M_L, S, M_S\rangle \rightarrow |L, S, J, M_J\rangle$$

Multiplet split

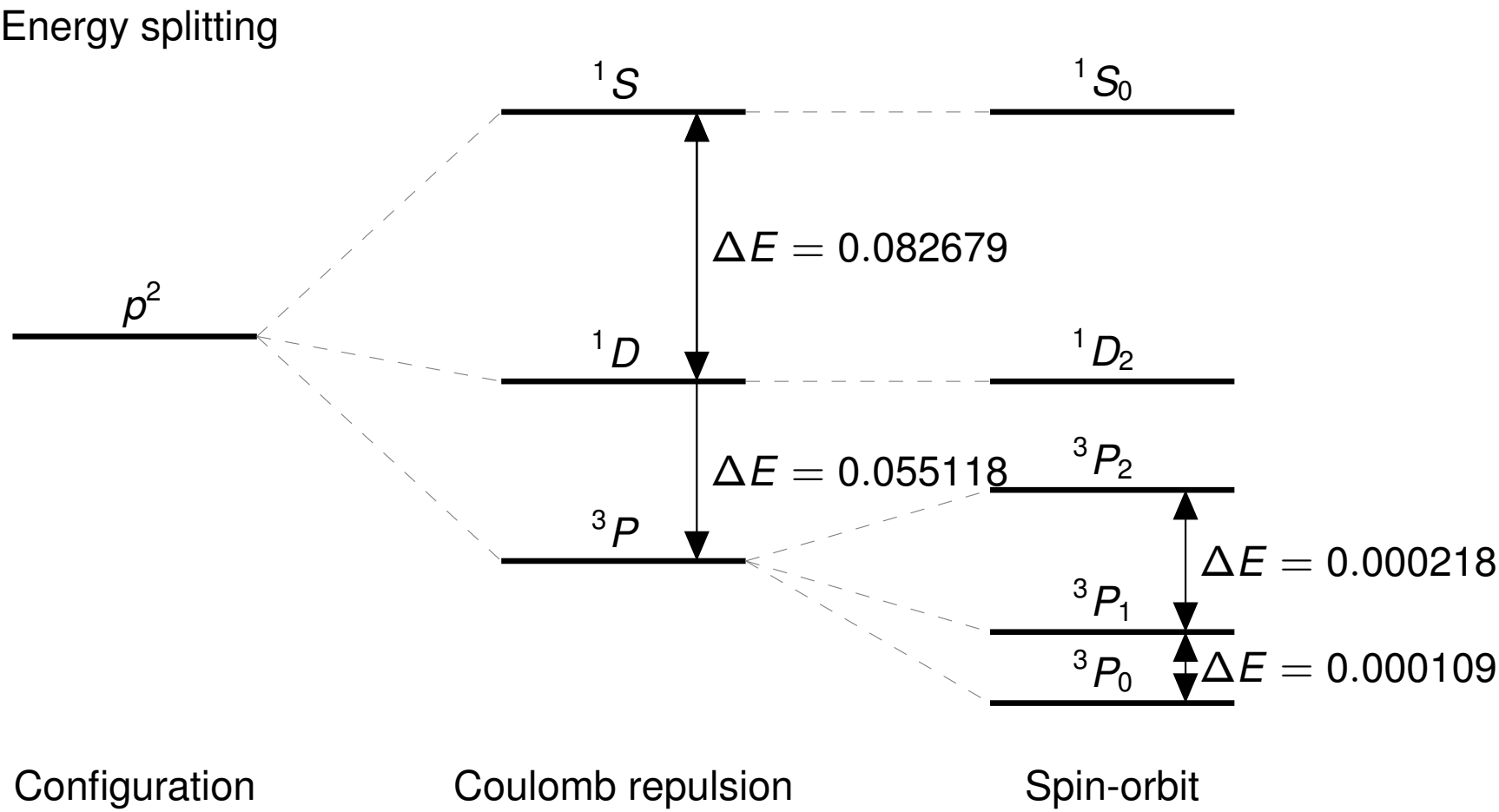
$$^{2S+1}L_J \quad \text{with} \quad J = L+S, L+S-1, \ldots, |L-S|$$

$$^3P \rightarrow {}^3P_2, {}^3P_1, {}^3P_0$$

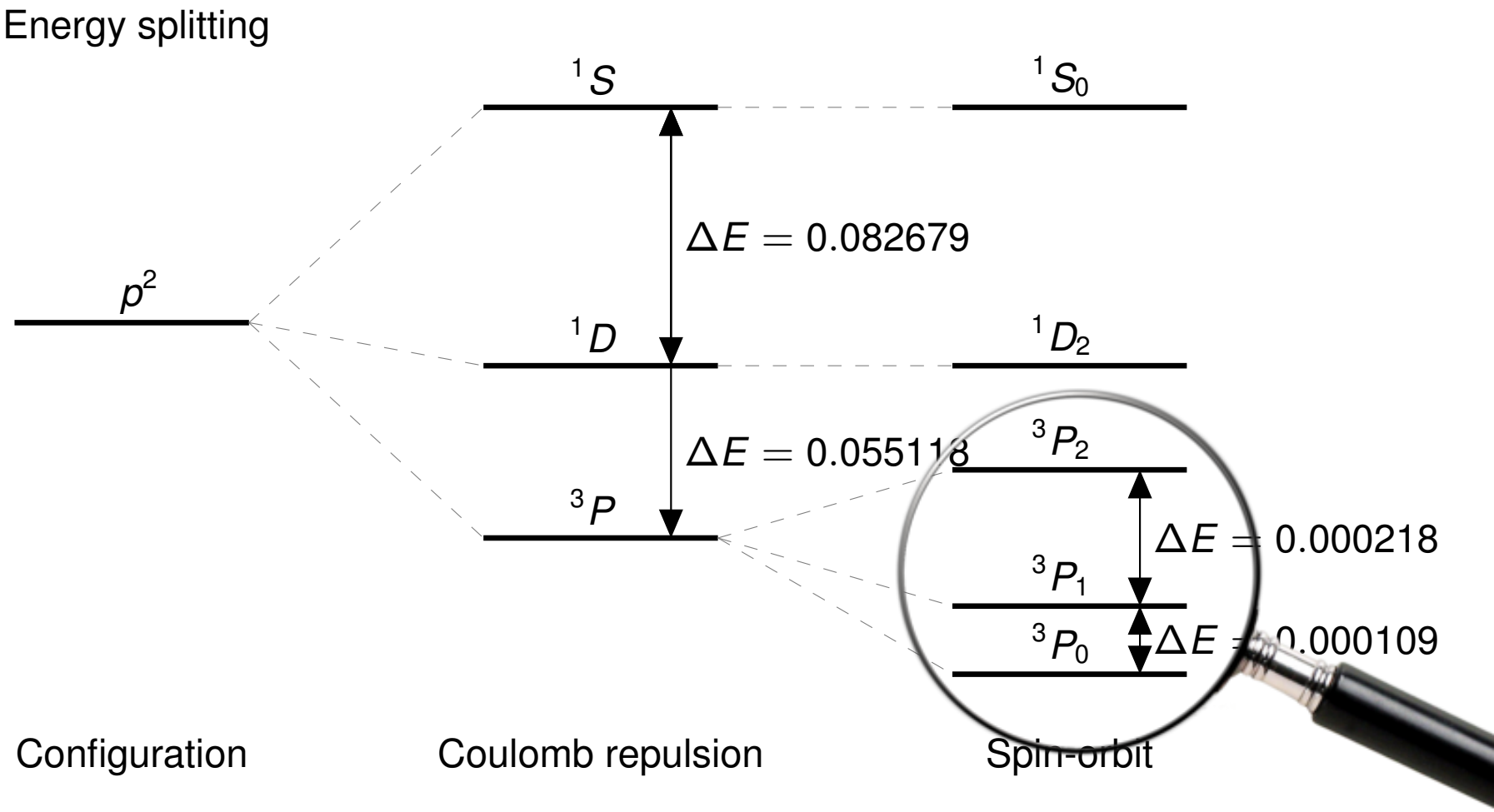
Eigen-energies

$$\boxed{E_{\mathrm{SO}} = A(nl, LS)\frac{1}{2}[J(J+1) - L(L+1) - S(S+1)]}$$

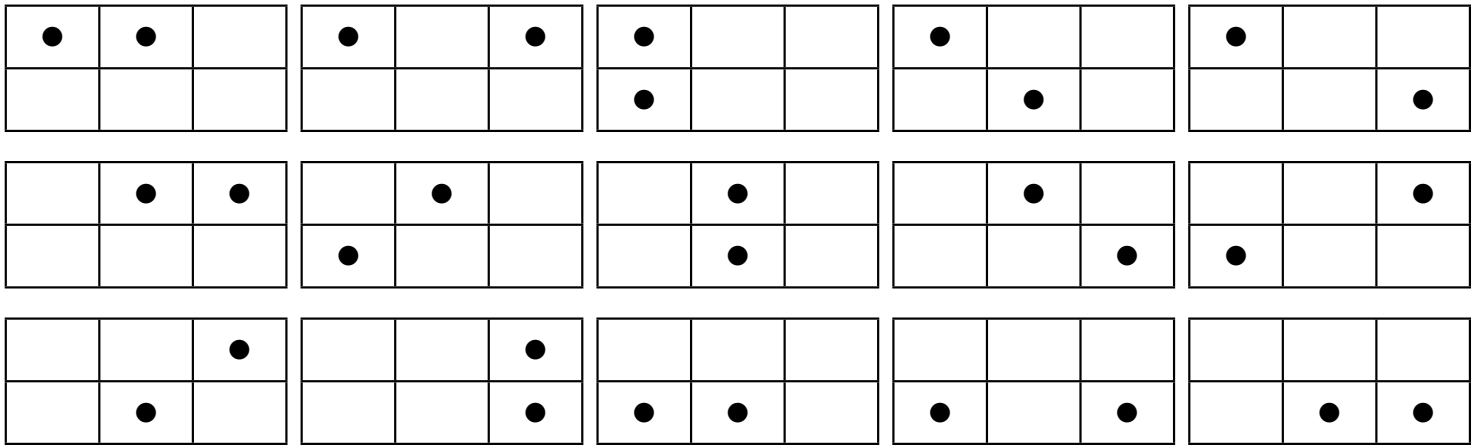
Spin-orbit coupling within multiplet terms



Spin-orbit coupling within multiplet terms



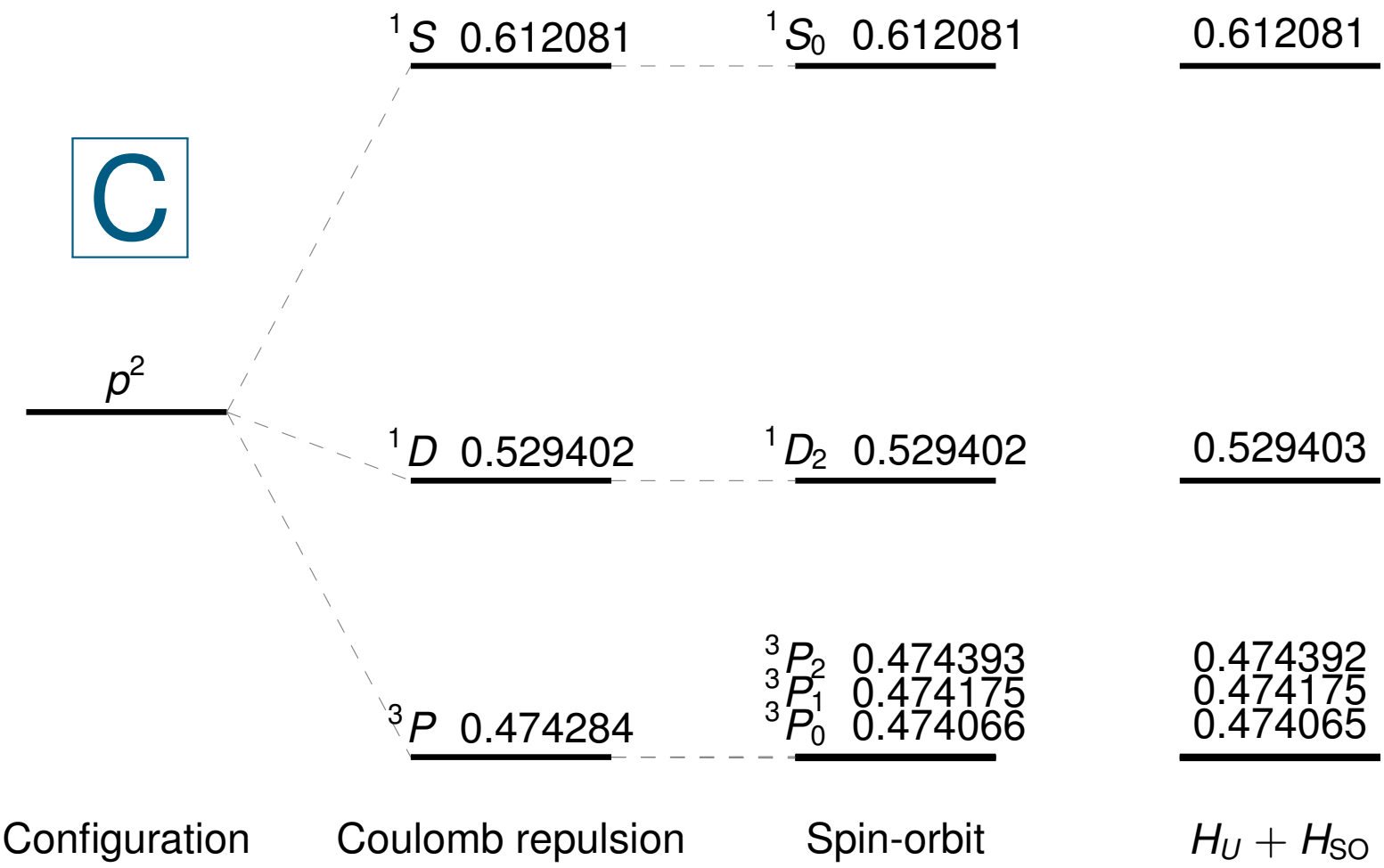
Spin-orbit coupling within entire shell



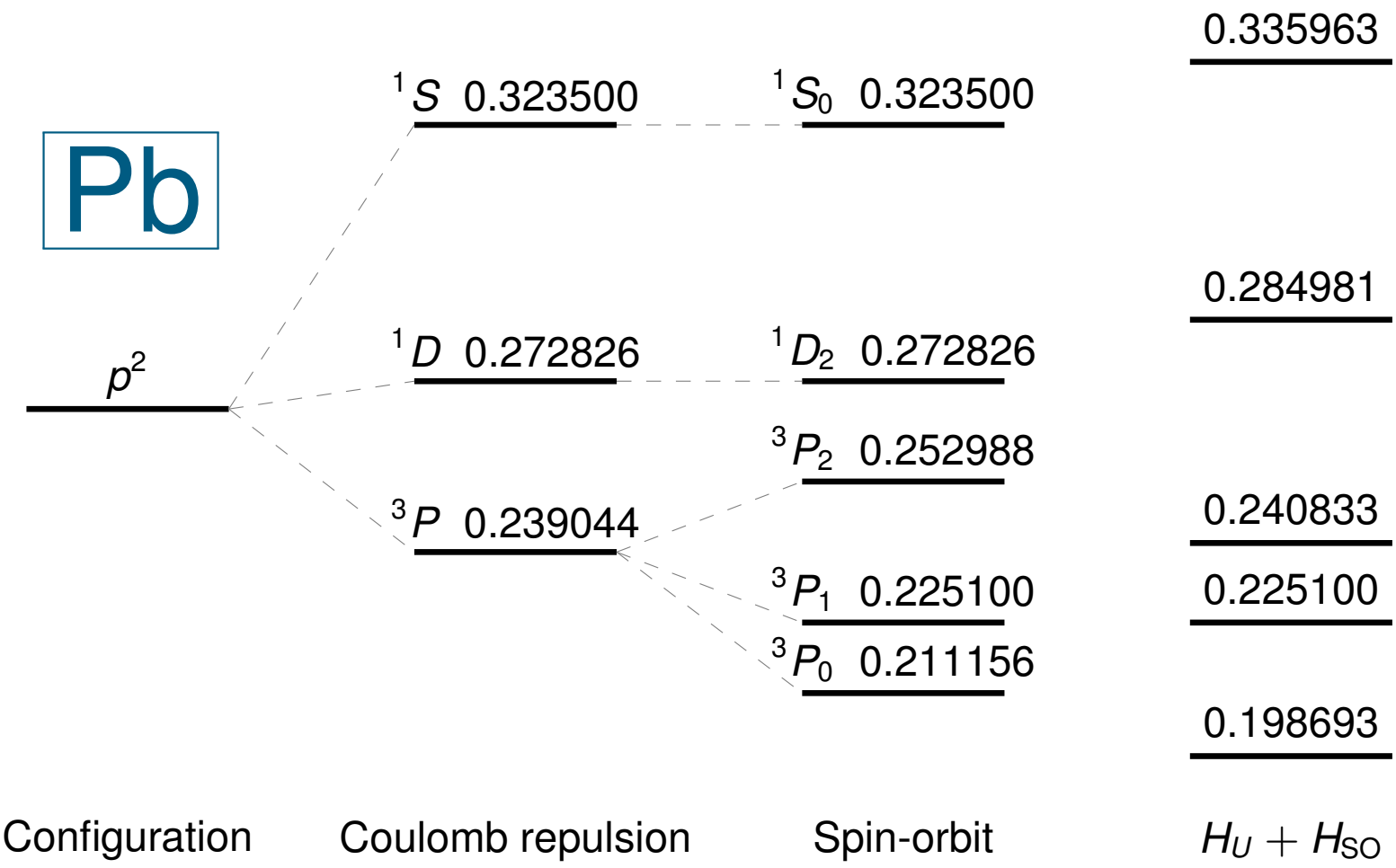
$$H_{\mathrm{SO}} = \sum_{i=1}^{N} \xi(r_i)\boldsymbol{\ell}_i \cdot \mathbf{s}_i \quad \longrightarrow \quad H_{\mathrm{SO}} = \sum_{\alpha,\beta} V_{\alpha\beta} c_\alpha^\dagger c_\beta$$

$$V_{\alpha\beta} = \langle \alpha | \, \xi(r)\boldsymbol{\ell} \cdot \mathbf{s} \, | \beta \rangle$$

Spin-orbit coupling within entire shell



Spin-orbit coupling within entire shell



Conclusion

1. We implemented Numerov's method with logarithmic grid to solve the one-electron problem and obtained very accurate solutions.
2. We solved the many-electron problem using self-consistent field approximation.
3. Based on SCF calculation, we constructed atomic multiplet states, which are the many-electron eigen-states in atoms.
4. Finally we introduced the spin-orbit coupling, where we see the spectral lines further split into finer structures.

Thank You!

Special thanks to:

- Prof. Dr. Erik Koch
- Dr. Hermann Ulm
- German Research School for Simulation Sciences
- Forschungszentrum Jülich GmbH

Backup Materials

Numerov's method

Finite difference

$$\frac{d^2\tilde{u}}{dx^2} = \frac{\tilde{u}_{i+1} - 2\tilde{u}_i + \tilde{u}_{i-1}}{\Delta x^2} + \mathcal{O}(\Delta x^2)$$

Numerov's method

$$\frac{d^2\tilde{u}}{dx^2} = \frac{\tilde{u}_{i+1} - 2\tilde{u}_i + \tilde{u}_{i-1}}{\Delta x^2} - \frac{1}{12}\frac{\tilde{u}''_{i+1} - 2\tilde{u}''_i + \tilde{u}''_{i-1}}{\Delta x^2}\Delta x^2 + \mathcal{O}(\Delta x^4)$$

Use the original ODE

$$\tilde{u}''_i = -2k_i^2\tilde{u}_i \quad \text{and} \quad k_i^2 \equiv r_i^2 E - r_i^2 V(r_i) - \frac{1}{2}\left(l + \frac{1}{2}\right)^2$$

3-point recursion!

$$\tilde{u}_{i\pm1} = \frac{(2 - \frac{5\Delta x^2}{3}k_i^2)\tilde{u}_i - (1 + \frac{\Delta x^2}{6}k_{i\mp1}^2)\tilde{u}_{i\mp1}}{1 + \frac{\Delta x^2}{6}k_{i\pm1}^2}$$

Slater-Condon parameters

$$R^{(k)}(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) = \int_0^\infty dr_1 \int_0^\infty dr_2 \, \overline{u_{n_1 l_1}}(r_1) \overline{u_{n_2 l_2}}(r_2) \frac{r_<^k}{r_>^{k+1}} u_{n_3 l_3}(r_2) u_{n_4 l_4}(r_1)$$

If $r_1 \leq r_2$,

$$r_< = r_1, \quad r_> = r_2$$

If $r_1 > r_2$,

$$r_< = r_2, \quad r_> = r_1$$

$$R^{(k)}(n_1 l_1, n_2 l_2, n_3 l_3, n_4 l_4) =$$

$$\int_0^\infty dr_1 \overline{u_{n_1 l_1}}(r_1) u_{n_4 l_4}(r_1) \left[\frac{1}{r_1^{k+1}} \int_0^{r_1} dr_2 \, r_2^k \overline{u_{n_2 l_2}}(r_2) u_{n_3 l_3}(r_2) + r_1^k \int_{r_1}^\infty dr_2 \, \frac{1}{r_2^{k+1}} \overline{u_{n_2 l_2}}(r_2) u_{n_3 l_3}(r_2) \right]$$

Gaunt coefficients

$$A^{(k)}(l_1 m_1, l_2 m_2, l_3 m_3, l_4 m_4) =$$

$$\sum_{\mu=-k}^{k} \int_0^{2\pi} d\phi_1 \int_0^{\pi} d\theta_1 \sin\theta_1 \overline{Y_{l_1 m_1}}(\theta_1, \phi_1) \overline{Y_{k\mu}}(\theta_1, \phi_1) Y_{l_4 m_4}(\theta_1, \phi_1)$$

$$\int_0^{2\pi} d\phi_2 \int_0^{\pi} d\theta_2 \sin\theta_2 \overline{Y_{l_2 m_2}}(\theta_2, \phi_2) Y_{k\mu}(\theta_2, \phi_2) Y_{l_3 m_3}(\theta_2, \phi_2)$$

Gaunt coefficients

$$g^{(k)}_{m_1 m_2} = \langle l_1 m_1 | \, k\mu \, | l_2 m_2 \rangle$$

Gaunt coefficients

Recursion relation

$$\langle l_1 m_1 |\, k\mu \,| l_2 m_2 \rangle =$$

$$a \langle l_1 + 1, m_1 |\, k-1, \mu \,| l_2 m_2 \rangle + b \langle l_1 - 1, m_1 |\, k-1, \mu \,| l_2 m_2 \rangle + c \langle l_1 m_1 |\, k-2, \mu \,| l_2 m_2 \rangle$$

$$a = \sqrt{\frac{(2k+1)(2k-1)(l_1+m_1+1)(l_1-m_1+1)}{(k+\mu)(k-\mu)(2l_1+3)(2l_1+1)}}$$

$$b = \sqrt{\frac{(2k+1)(2k-1)(l_1+m_1)(l_1-m_1)}{(k+\mu)(k-\mu)(2l_1+1)(2l_1-1)}}$$

$$c = -\sqrt{\frac{(2k+1)(k+\mu-1)(k-\mu-1)}{(k+\mu)(k-\mu)(2k-3)}}$$

Base case

$$\langle l_1 m_1 |\, 00 \,| l_2 m_2 \rangle = \frac{1}{\sqrt{4\pi}} \delta_{l_1 l_2} \delta_{m_1 m_2}$$

Ladder operator techniques

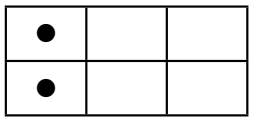
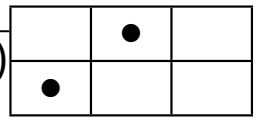
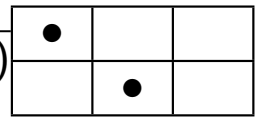
Ladder operators

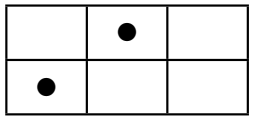
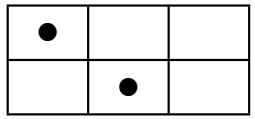
$$L_\pm |lm\rangle = \alpha^\pm_{lm} |l, m \pm 1\rangle$$

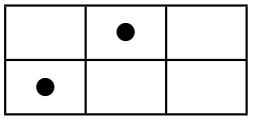
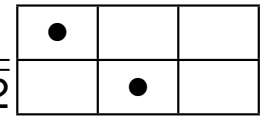
$$\alpha^+_{lm} = \sqrt{(l+m+1)(l-m)}$$

$$\alpha^-_{lm} = \sqrt{(l+m)(l-m+1)}$$

Express eigen-vectors in terms of our 15 basis vectors

L_-  $= \sqrt{(1+1)(1-1+1)}$  $+ \sqrt{(1+1)(1-1+1)}$ 

$L_- |2,2,0,0\rangle =$ $\sqrt{2}$  $+$ $\sqrt{2}$ 

$|2,1,0,0\rangle =$ $\frac{1}{\sqrt{2}}$  $+$ $\frac{1}{\sqrt{2}}$ 

$|2,1,0,0\rangle = \frac{1}{\sqrt{2}} c^\dagger_{1\downarrow} c^\dagger_{0\uparrow} |0\rangle + \frac{1}{\sqrt{2}} c^\dagger_{0\downarrow} c^\dagger_{1\uparrow} |0\rangle$