

Special Topics on Precision Measurement in Atomic Physics: Lecture 7

High Precision Results for Nonrelativistic Energies: Lithium

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LITHIUM WAVE FUNCTIONS

Construction of wave functions

The basis set is constructed from the terms

$$\begin{aligned} \phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \\ &\times \mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \chi_1, \end{aligned} \quad (1)$$

where

$$\begin{aligned} \mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM} &= r_1^{l_1} r_2^{l_2} r_3^{l_3} \sum_{m_i} \langle l_1 m_1; l_2 m_2 | l_{12} l_{12}; l_{12} M_{12} \rangle \langle l_{12} M_{12}; l_3 m_3 | l_{12} l_3; LM \rangle \\ &\times Y_{l_1 m_1}(\mathbf{r}_1) Y_{l_2 m_2}(\mathbf{r}_2) Y_{l_3 m_3}(\mathbf{r}_3) \end{aligned} \quad (2)$$

denotes a vector-coupled product of spherical harmonics for the three electrons to form a state of total angular momentum L .

The spin function is now more complicated, and not unique. There are two possible coupling schemes:

$$\text{spin}(1/2) + \text{spin}(1/2) \rightarrow \text{spin}(0) \quad \text{i.e. singlet}$$

$$\text{spin}(0) + \text{spin}(1/2) \rightarrow \text{spin}(1/2)$$

OR

$$\text{spin}(1/2) + \text{spin}(1/2) \rightarrow \text{spin}(1) \quad \text{i.e. triplet}$$

$$\text{spin}(1) + \text{spin}(1/2) \rightarrow \text{spin}(1/2)$$

In the former (singlet) case

$$\chi_1 = \alpha(1)\beta(2)\alpha(3) - \beta(1)\alpha(2)\alpha(3) \quad (3)$$

is the spin function with the spin angular momentum 1/2.

Our work shows that the exclusion of the second linearly independent spin function does not affect the final convergence of energy eigenvalues.

In (1), the $\mathcal{Y}_{(l_1 l_2) l_{12}, l_3}^{LM}$ functions include the lowest powers of r_1 , r_2 , and r_3 in order to ensure correct behavior of the wave function as $r_i \rightarrow 0$.

The variational wave function is a linear combination of the functions ϕ antisymmetrized by the three-particle antisymmetrizer

$$\mathcal{A} = (1) - (12) - (13) - (23) + (123) + (132). \quad (4)$$

For a given angular momentum L , the angular coupling for the three electrons is

$$\begin{aligned} (l_1, l_2, l_3) &= (0, 0, 0)_A \text{ for } S \text{ states} \\ (l_1, l_2, l_3) &= (0, 0, 1)_A \text{ and } (0, 1, 0)_B \text{ for } P \text{ states} \\ (l_1, l_2, l_3) &= (0, 0, 2)_A \text{ and } (0, 1, 1)_B \text{ for } D \text{ states, etc..} \end{aligned}$$

The inclusion of block $(0, 1, 0)_B$ in the P state basis sets, which describes the core polarization, is crucial in obtaining adequate convergence.

For small basis sets, the gain is barely detectable. However, it becomes essential when the basis sets become large. With only block $(0, 0, 1)_A$ included, the energy eigenvalue apparently converges to an incorrect value $-7.410\,136\,34$ a.u., even if the size of the basis set becomes as large as 1500 terms.

Recall that a similar situation occurs in the two-electron case when the mass polarization operator $\nabla_1 \cdot \nabla_2$ is included explicitly in the Hamiltonian for the $sp - ps$ exchange term.

This illustrates that experiments with small basis sets may lead to conclusions that are incorrect as basis sets become large.

It also illustrates the need to search for all potentially important class of terms. In the case of the P states, the $(0, 0, 1)_A$ and $(0, 1, 0)_B$ terms differ only in their exponential scale factors. Although either set by itself becomes asymptotically complete in the limit of infinite basis sets, a finite sequence of calculations may give a false impression of convergence to an energy that is too high.

Inclusion of just a few $(0, 1, 0)_B$ terms for the P states has an immediate and dramatic effect for large basis sets. A systematic search for other possible such terms did not yield a further significant lowering of the energy. However, this is by no means a proof that none exist, only that they were searched for and none found. In the case of the 3^2D state, the inclusion of a $(0, 2, 0)$ block does not change the pattern of convergence.

In generating the finite basis sets, all terms from (1) are nominally included such that

$$j_1 + j_2 + j_3 + j_{12} + j_{23} + j_{31} \leq \Omega, \quad (5)$$

and the convergence of the eigenvalues studied as Ω is progressively increased.

However, terms which may potentially cause near linear dependences should be excluded. For example, if $l_1 = l_2$ and $\alpha \approx \beta$, then terms with $j_1 > j_2$ should be omitted, as well as terms with $j_1 = j_2$ when $j_{23} > j_{31}$. The presence of the near linear dependences in the basis set can be detected by diagonalizing the positive definite overlap matrix to see if there is an abnormally small or negative eigenvalue.

MULTIPLE BASIS SETS

For the two-electron case it was sufficient to double (or triple) the basis set to obtain adequate convergence and avoid linear dependence.

For lithium, the total basis set is divided into several sectors with different scale factors α , β , and γ . These are then separately optimized for each sector.

This strategy dramatically improves the accuracy for a given total number of terms in the basis set. However, the details are more complicated.

instead of simply duplicating the terms in each block and assigning independent scale factors as in the helium calculations, the first block $(0, 0, L)_A$ is divided into five sectors according to correlations among the three electrons as follows:

$$\begin{aligned} \text{Sector 1 :} & \quad \text{all } j_{12}, \quad j_{23} = 0, \quad j_{31} = 0 \\ \text{Sector 2 :} & \quad \text{all } j_{12}, \quad j_{23} = 0, \quad j_{31} \neq 0 \\ \text{Sector 3 :} & \quad \text{all } j_{12}, \quad j_{23} \neq 0, \quad j_{31} = 0 \\ \text{Sector 4 :} & \quad j_{12} = 0, \quad j_{23} \neq 0, \quad j_{31} \neq 0 \\ \text{Sector 5 :} & \quad j_{12} \neq 0, \quad j_{23} \neq 0, \quad j_{31} \neq 0. \end{aligned}$$

This scheme has an obvious significance in terms of which correlations are contained in each sector.

A complete optimization of the nonlinear parameters leads to a natural division of the basis set into these five sectors with quite different distance scales. Therefore, a complete optimization is important not only for improving the variational eigenvalues, but also for preserving the numerical stability of the wave function, especially when Ω is large.

The complete basis sets thus contain five sectors for S -states, and six sectors for P - and D - states when the $(0, 1, 0)_B$ or $(0, 1, 1)_B$ blocks are included. Finally, the size of each sector is separately controlled by assigning to each an Ω_i value according to

$$\begin{aligned} \{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5\} &= \{\Omega, \Omega, \Omega, \Omega, \Omega\}, \quad L = 0 \\ \{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5, \Omega_6\} &= \{\Omega, \Omega, (\Omega, 7)_{\min}, (\Omega, 7)_{\min}, (\Omega, 7)_{\min}, \Omega - 2\}, \quad L = 1 \\ \{\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5, \Omega_6\} &= \{\Omega, \Omega, \Omega, \Omega, \Omega, (\Omega - 2, 3)_{\min}\}, \quad L = 2, \end{aligned}$$

where $(a, b)_{\min}$ denotes $\min(a, b)$. The resulting truncations of the basis set in the indicated sectors have been carefully studied to verify that they do not significantly affect the eigenvalue convergence pattern.

NONRELATIVISTIC EIGENVALEUS

As before, the nonlinear parameters are optimized by calculating analytically the derivatives

$$\frac{\partial E}{\partial \alpha} = 2\langle \Psi | H | \frac{\partial \Psi}{\partial \alpha} \rangle - 2E \langle \Psi | \frac{\partial \Psi}{\partial \alpha} \rangle, \quad (6)$$

where α represents any nonlinear parameter, H is the Hamiltonian of lithium, and the normalization $\langle \Psi | \Psi \rangle = 1$ is assumed. Newton's method is used to locate the zero's of the first derivatives. Provided that the initial α_i , β_i , and γ_i are chosen close to a minimum, the procedure converges in a few iterations.

The following table lists the results for the nonrelativistic energies, together with a detailed account of the convergence process as the size of the basis set is enlarged.

Nonrelativistic energies for the $1s^2 2s^2 S$, $1s^2 2p^2 P$, and $1s^2 3d^2 D$ states of lithium, in atomic units.

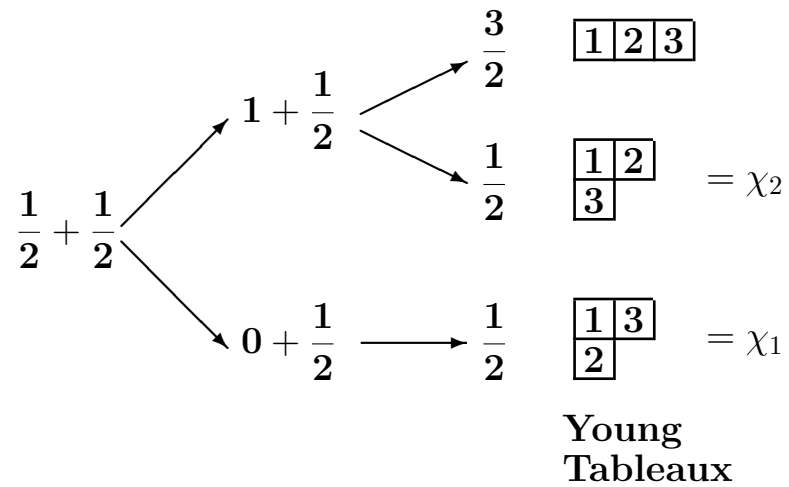
Ω	No. of terms	$E(\Omega)$	$R(\Omega)$
$1s^2 2s^2 S$			
2	18	-7.477 311 711 30	
3	50	-7.477 984 835 87	
4	120	-7.478 052 568 65	9.938
5	256	-7.478 059 384 23	9.938
6	502	-7.478 060 203 73	8.317
7	918	-7.478 060 310 46	7.678
8	1589	-7.478 060 321 56	9.611
∞		-7.478 060 323 10(31)	
$1s^2 2p^2 P$			
2	19	-7.409 722 805 8	
3	55	-7.410 100 606 3	
4	138	-7.410 150 289 3	7.604
5	306	-7.410 155 458 5	9.611
6	622	-7.410 156 380 9	5.604
7	1174	-7.410 156 500 2	7.733
8	1715	-7.410 156 518 4	6.540
∞		-7.410 156 521 8(13)	
$1s^2 3d^2 D$			
2	19	-7.335 271 380 14	
3	57	-7.335 484 754 84	
4	148	-7.335 520 359 81	5.993
5	340	-7.335 523 158 86	12.720
6	586	-7.335 523 488 10	8.502
7	1002	-7.335 523 534 71	7.064
8	1673	-7.335 523 540 35	8.253
∞		-7.335 523 541 10(43)	
<hr/>			
hline			

COMPARISONS WITH OTHER CALCULATIONS

Table 1: Comparison with other calculations for the nonrelativistic energies of lithium, in atomic units.

Author	Method	Ref.	$1s^2 2s^2 S$	$1s^2 2p^2 P$
Larsson (68)	100-term Hy.	[11]	-7.478 025	
Ahlenius and Larsson (73)	78-term Hy.	[12]		-7.409 99
Sims and Hagstrom (75)	150, 120-term CI-Hy.	[13]	-7.478 023	-7.410053
Ahlenius and Larsson (78)	97-term Hy.	[14]		-7.410 078
Muszyńska <i>et al.</i> (80)	139, 120-term CI-Hy.	[15]	-7.478 044	-7.410 097
Ho (81)	92-term Hy.	[16]	-7.478 031	
Pipin and Woźnicki (83)	170-term CI-Hy.	[17]	-7.478 044	-7.4101 06
King and Shoup (86)	352-term Hy.	[4]	-7.478 058	
Kleindienst and Beutner (89)	310-term Hy.	[18]	-7.478 058 24	
King (89)	602-term Hy.	[5]	-7.478 059	
King and Bergsbaken (90)	296-term Hy.	[19]	-7.478 059 53	
Jitrik and Bunge (91)	Extrapolated CI	[20]	-7.478 062 4(7)	
Chung <i>et al.</i> (91-93)	Full core plus corr.	[9]	-7.478 059 7(9)	-7.410 157 8(9)
McKenzie and Drake (91)	1134-term Hy.	[6]	-7.478 060 326(10)	
Pipin and Bishop (92)	1618, 1454, 1478 CI-Hy.	[7]	-7.478 060 1	-7.410 155 4
Lüchow and Kleindienst (92)	976-term Hy.	[8]	-7.478 060 25	
Tong <i>et al.</i> (93)	Extrapolated MCHF	[21]	-7.478 060 9	-7.410 153 1
Present work			-7.478 060 323 10(31)	-7.410 156 521 8(1)

Alternative Spin Coupling Chains.



$$\chi_1 = [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\alpha(3)$$

$$\chi_2 = 2\alpha(1)\alpha(2)\beta(3) - [\alpha(1)\beta(2) + \beta(1)\alpha(2)]\alpha(3)$$

The complete wave function is

$$\psi = \mathcal{A}(\phi_1\chi_1 + \phi_2\chi_2)$$

where \mathcal{A} is the total antisymmetrizer

$$\mathcal{A} = e - (12) - (13) - (23) + (123) + (132)$$

Question: Do we need both χ_1 and χ_2 ?

Larsson's Argument

Sven Larsson, Phys. Rev **169**, 59 (1968).

Suppose that a function $\psi_1 = \mathcal{A}\{\phi \cdot (\alpha\beta - \beta\alpha)\alpha\}$ is contained in the basis set. Now we can generate new functions by permuting the labels in ϕ . The key point is that this is equivalent to permuting the spin labels after antisymmetrization, multiplied by the original ϕ . For example

$$\psi' = \mathcal{A}\{(13)\phi \cdot (\alpha\beta - \beta\alpha)\alpha\} = -\mathcal{A}\{\phi \cdot (\alpha\beta\alpha - \alpha\alpha\beta)\}$$

and

$$\psi'' = \mathcal{A}\{(23)\phi \cdot (\alpha\beta - \beta\alpha)\alpha\} = -\mathcal{A}\{\phi \cdot (\alpha\alpha\beta - \beta\alpha\alpha)\}$$

Since there are only two doublet spin functions, ψ_1 , ψ' , and ψ'' are not all linearly independent. Choose ψ_1 and ψ_{12} , where

$$\begin{aligned}\psi_{12} = \psi' - \psi'' &= \mathcal{A}\{[(13) - (23)]\phi \cdot (\alpha\beta\alpha - \beta\alpha\alpha)\} \\ &= \mathcal{A}\{\phi \cdot (2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha)\}\end{aligned}$$

Note that if ϕ has exact (12) symmetry, then

$$[(13) - (23)]\phi \equiv 0$$

For example, if

$$\phi(r_1, r_2, r_3) = \phi_{1s}(r_1) \phi_{1s}(r_2) \phi_{2s}(r_3)$$

then $[(13) - (23)]\phi \equiv 0$.

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