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Studies of Off-Diagonal Hypervirial Constraints

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Further investigation is made on the use of off-diagonal hypervirial theorems as constraints. Firstly, it is found that an energy-independent off-diagonal constraint is not useful in improving calculation of transition probabilities. Secondly, when the approximate wavefunction is flexible enough, iteration on the transition energy converges very rapidly. Finally the study is extended to the isoelectronic species Li^+ and Be^{+2}.

In a recent paper, Chong and Benston [1] extended the method of constrained variations to off-diagonal constraints. In applying the method to the calculation of dipole length M_1, dipole velocity M_2, and dipole acceleration M_3, they assumed a constant transition energy ΔE.

With the recent advances in the method of solving constrained secular equations [2, 3], we have made further studies on the use of off-diagonal hypervirial theorems (ODHT) as constraints. In all of the cases studied here, the ^1P upper-state wavefunctions are approximated by Eckart-type functions [4].

Energy-Independent ODHT

Coulson [5] suggested the use of energy-independent ODHT as constraints. A particular application is to formulate the constraint as

$$C = M_2^2 - M_1 M_3 . \tag{1}$$

The constraint operator for this C is straightforward to construct, and is actually a diagonal constraint operator.

Such a constraint is tested on the five-term approximate wavefunction used by Chong and Benston [1] for the ^1S ground state of helium. The results are somewhat disappointing. We find that the constrained wavefunction gives the values of 0.46238, 0.42697, and 0.39427 for M_1, M_2, and M_3 (in atomic units) respectively, compared to the exact value of 0.42078 [6]. In the first place, the constraint in Eq. (1) fails to remove the undesirable ambiguity in the calculation of transition moments. Secondly, the best moment (M_2 in this example) from the constrained wavefunction deviates more from the exact value than the free-variational result of 0.42155 [1] does.

Iteration on the Transition Energy

For each approximate wavefunction, Chong and Benston [1] assumed that the transition energy ΔE is constant, at the free-variational value. Since the constraints cause a small sacrifice in the energy of the ground-state wavefunctions, the constrained functions they obtained do not, strictly speaking, satisfy the ODHT. Therefore, the effect of iterating on ΔE is studied in the present work.

Since the sacrifice in energy on constraining is generally small, it is surprising to discover that, for some of the constraints on wavefunctions with few (five or six) terms, the iteration on ΔE fails to converge. On the other hand, when the approximate wavefunction is flexible enough, the iteration converges in a few cycles.

The wavefunction for the ground state of He used here is of the same form as the seven-term function of Chong and Benston [1]. The orbital exponents, which have been better optimized, are presented in Table 1. The results of our investigations are shown in Table 2. Comparing with the results based on the assumption of constant ΔE, we see that the effect of iterating on ΔE is small.

Table 1. *Orbital exponents of Slater-type atomic orbitals used in seven-term wavefunctions of the form:* $1s^2 + 1s2s + 1s3s + 2s^2 + 2s3s + 3s^2 + 2p^2$

Species	$1s$	$2s$	$3s$	$2p$
He	1.5394	1.8189	2.0170	2.4608
Li^+	2.5346	3.5180	3.6041	3.9243
Be^{+2}	3.4330	4.0768	4.7897	5.3869

Table 2. *Results of constrained variations of seven-term approximate wavefunctions for the ^1S ground states of two-electron atomic system (see text). The results for the assumption of constant ΔE are given in parentheses*

System	Constrain	E	M_1	M_2	M_3
He	none	− 2.897902	0.40362	0.41758	0.40195
	$M_1 = M_2$	− 2.897090	0.42006	0.42006	0.40726
		(− 2.897138)	(0.41956)	(0.41956)	(0.40626)
	$M_1 = M_3$	− 2.897897	0.40260	0.41723	0.40260
		(− 2.897897)	(0.40260)	(0.41723)	(0.40260)
	$M_2 = M_3$	− 2.897267	0.40232	0.41484	0.41484
		(− 2.897238)	(0.40230)	(0.41443)	(0.41443)
	$M_1 = M_2 = M_3$	− 2.896630	0.41759	0.41759	0.41759
		(− 2.896650)	(0.41663)	(0.41663)	(0.41663)
Exact	none	− 2.903724[a]		0.42078[b]	
Li^+	none	− 7.272961	0.31255	0.31380	0.30345
	$M_1 = M_2 = M_3$	− 7.271280	0.31164	0.31164	0.31164
Exact	none	− 7.279913[a]		0.316_1[c]	
Be^{+2}	none	−13.647883	0.23930	0.25685	0.25387
	$M_1 = M_2 = M_3$	−13.645232	0.24573	0.24573	0.24573
Exact	none	−13.655566[a]		0.246_4[c]	

[a] Ref. [7]. – [b] Ref. [6]. – [c] Ref. [8].

Extension to Li^+ and Be^{+2}

The same approach of iterating on the transition energy is extended to the corresponding ^1S to ^1P transition in Li^+ and Be^{+2}.

The optimized orbital exponents for seven-term wavefunctions of the ground states are listed in Table 1. The results of free variations and constrained variations are summarized[1] in Table 2.

It is encouraging to find that such relatively simple seven-term wavefunctions can lead to transition moments which are not only unambiguous, but also in good agreement with those resulting from extensive variational calculations [8].

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[1] Results on single constraints as well as those on six-term wavefunctions will be included in the Ph. D. thesis (in preparation) of C. P. Yue.