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Ludwik Adamowicz and E. A. McCullough Jr.

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[b] School of Physics, Georgia Institute of Technology.

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A numerical multiconfiguration self-consistent-field method for diatomic molecules

Ludwik Adamowicz[a] and E. A. McCullough, Jr.

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322
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The multiconfiguration self-consistent-field (MCSCF) method seeks a truncated configuration interaction (CI) expansion of the electronic wave function which is energy optimized with respect to both the CI coefficients and the orbitals. Although there are significant differences between many of the existing implementations of the MCSCF method,[1] they all share a common feature: the orbitals are represented by truncated basis set expansions. This basis set truncation introduces an additional source of error, which can vary from negligible to serious, depending on the particular basis set and application.

We wish to communicate what we believe are the first numerical solutions of the MCSCF problem for diatomic molecules. Our approach, which yields an essentially exact MCSCF wave function for a given configuration list, is based on a partial-wave expansion of the orbitals in prolate spheroidal coordinates. Much of the methodology is identical to that developed for the single configuration problem, so we refer the reader to our previous publications for details.[2] Here we merely mention a few aspects especially pertinent to the MCSCF problem.

We employ a Fock operator formalism. The Fock equations for each orbital are solved sequentially, explicitly including the off-diagonal Lagrange multipliers. The Hamiltonian matrix is then diagonalized, and two-by-two orbital rotations are performed to obtain a near minimum energy solution. These steps are iterated to convergence. Our approach is very similar to the numerical atomic MCSCF method developed by Fischer,[3] and to the basis set method implemented by Das and Wahl.[1(b)]

Since no exact MCSCF solution is available for any molecule, atoms provide the most rigorous test of our method. Fischer has reported detailed numerical atomic MCSCF results for C^{2+} (^1S) in the two configuration approximation $1s^2(2s^2 + 2p^2)$.[4] Table I compares our results with hers. We treat the ion as a heteronuclear diatomic molecule with zero charge on one nucleus and an arbitrary internuclear distance (0.5 bohr in this case). Note that only $C_{\infty v}$ symmetry is being utilized. In particular, the atomic configuration $1s^2 2p^2$ becomes two distinct configurations $1s^2 2p\sigma^2$ and $1s^2 2p\pi^2$.

TABLE I. MCSCF results (a. u.) for C^{2+} (^1S).

	Numerical atomic[a]	Numerical molecular	
E	-36.48096		-36.48096
ϵ_{1s}	-12.62367		-12.62366
ϵ_{2s}	-1.76616		-1.76621
ϵ_{2p}	-2.07529	σ:	-2.07451
		π:	-2.07450
$\langle 1/r \rangle_{1s}$	5.70343		5.70338
$\langle 1/r \rangle_{2s}$	1.01782		1.01788
$\langle 1/r \rangle_{2p}$	0.97526	σ:	0.97525
		π:	0.97525
$\langle r^2 \rangle_{1s}$	0.09420		0.09421
$\langle r^2 \rangle_{2s}$	2.16639		2.16635
$\langle r^2 \rangle_{2p}$	1.91268	σ:	1.91286
		π:	1.91286

[a] Reference 4.

TABLE II. MCSCF results (a. u.) for LiH($X {}^1\Sigma$) at $R = 3.015a_0$.

	E	μ	Θ_{CMN}
$1\sigma^2(2\sigma^2 + 3\sigma^2 + 4\sigma^2 + 1\pi^2)$	-8.02127	-2.305	-3.13
15 Configuration average field[a]	-8.02131	-2.317	-3.12

[a] Interpolated basis set results of Ref. 5.

TABLE III. MCSCF results (a. u.) for LiH($B\,^1\Pi$) at $R = 4.5a_0$.

	E	μ	θ_{CMN}
$1\sigma^2\,2\sigma1\pi$	-7.86440	0.200	6.60
$1\sigma^2\,(2\sigma1\pi + 3\sigma2\pi)$	-7.86523	0.183	6.60
$1\sigma^2\,(2\sigma1\pi + 3\sigma2\pi + 4\sigma3\pi)$	-7.86548	0.174	6.62
$1\sigma^2\,(2\sigma1\pi + 3\sigma2\pi + 4\sigma3\pi + 2\pi1\delta + 3\pi2\delta)^a$	-7.86566	0.152	6.59

[a]Basis set results of Ref. 5.

TABLE IV. MCSCF results (a. u.) for LiH($^3\Pi$) at $R = 3.76a_0$.

	E	μ	θ_{CMN}
$1\sigma^2\,2\sigma1\pi$	-7.87112	-0.187	5.99
$1\sigma^2\,(2\sigma1\pi + 3\sigma2\pi)$	-7.87266	-0.234	5.90
$1\sigma^2\,(2\sigma1\pi + 3\sigma2\pi + 4\sigma3\pi)$	-7.87324	-0.247	5.87
$1\sigma^2\,(2\sigma1\pi + 3\sigma2\pi + 4\sigma3\pi + 2\pi1\delta + 3\pi2\delta)^a$	-7.87336	-0.087	5.99

[a]Interpolated basis set results of Ref. 5.

The $2p\sigma$ orbital is not automatically orthogonal to $1s$ and $2s$, nor are the $2p\sigma$ and $2p\pi$ orbitals automatically rotationally equivalent. Their inequivalence is, in fact, a measure of the numerical error in our calculation. As Table I shows, this error is small. Overall, the agreement with the numerical atomic results is excellent.

For our initial application to molecules, we focused on LiH. In a pioneering MCSCF study, Docken and Hinze carried out a thorough investigation of several electronic states of LiH using a large $(23\sigma\,8\pi\,4\delta)$ Slater basis optimized for the $X^1\Sigma$ state at one internuclear distance.[5] Table II compares the energy, dipole moment, and quadrupole moment from our four configuration numerical MCSCF calculation with their 15 configuration, average field results for this state. The two sets are virtually identical.

The excited Π states are more interesting. For the $^1\Pi$ state (Table III), our numerical calculations with one, two, and three configurations appear to be converging nicely toward the five configuration basis set results, but there are clearly major discrepancies for the $^3\Pi$ state (Table IV). Our numerical dipole moment starts out far away from the basis set result, and the difference increases! A similar, but less dramatic, lack of convergence is seen in the quadrupole moment. Of course, the effect of the two omitted configurations must be considered, but their energetic contribution to the wave function is very small, and it is doubtful that they would reduce the dipole moment much below 0.2 a.u. Hence, there appears to be a substantial basis set error in the five configuration $^3\Pi$ electronic moments. This is most probably due to the lack of sufficiently diffuse $p\pi$ functions on H and/or $d\pi$ functions on Li which prevents the very diffuse π orbital from

polarizing properly toward the hydrogen.

The numerical MCSCF calculations reported here required from 5 to 30 min of CPU time on a VAX. These figures should be regarded as very generous upper limits, since the current version of the numerical MCSCF program is in no sense computationally optimized.

[a]Permanent address: Institute of Physical Chemistry, Polish Academy of Science, Warsaw, Poland.

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