

Method of Local Configuration Interaction Applied to Electronic Systems. Hydrogen Atom and Hydrogen Molecule Ion*

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The local configuration interaction method, a way to solve the Schrödinger equation without evaluating integrals, is applied to two electronic systems: the hydrogen atom and the hydrogen molecule ion. The exact energies are reproduced for both systems. The H_2^+ is treated both as a separable and nonseparable problem. The convergence to the exact energy is seen to be slower than for a variational calculation with the same basis.

INTRODUCTION

Recently a method for solving the Schrödinger equation without evaluating integrals was proposed.¹ With Hamiltonian H and wavefunction $\psi(\mathbf{x})$, approximated as a linear combination of N basis functions $\phi_i(\mathbf{x})$,

$$\psi(\mathbf{x}) = \sum_{i=1}^N c_i \phi_i(\mathbf{x}), \quad (1)$$

the energy E and coefficients c_i are determined from the N conditions,

$$(H^k - E^k)\psi(\mathbf{x})|_{\mathbf{x}=\mathbf{x}_0} = 0, \quad k = 1, 2, \dots, N. \quad (2)$$

The \mathbf{x}_0 denotes a particular (but arbitrary) point in the configuration space of H . The general method, in which the basis functions are unspecified, is called the local configuration interaction (CI) method. If the basis functions ϕ_i for $i \geq 2$ are generated from the first according to

$$\phi_i(\mathbf{x}) = H^{i-1}\phi_1(\mathbf{x}), \quad (3)$$

the technique is called the method of local moments.^{1,2} In practice, the energy E is determined as a root of the polynomial equation,

$$\det \begin{vmatrix} 1 & \phi_1(x_0) & \cdots & \phi_N(x_0) \\ E & H\phi_1(x_0) & & H\phi_N(x_0) \\ E^2 & H^2\phi_1(x_0) & & H^2\phi_N(x_0) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ E^N & H^N\phi_1(x_0) & \cdots & H^N\phi_N(x_0) \end{vmatrix} = 0. \quad (4)$$

A deficiency of the local methods is the lack of an

upper or lower bound theorem or any other convenient convergence theorem. Consequently the usefulness of the methods can only be gauged by example.

For harmonic oscillators the local moment method works quite well.^{1,3} Because of the completely different nature of the Coulomb potential $1/r$ from $\frac{1}{2}kx^2$, however, harmonic oscillators are not typical of atoms and molecules. This paper discusses the applicability of the local methods to atoms and molecules through the examples of the hydrogen atom and the hydrogen molecule ion.

HYDROGEN ATOM

Consider first attempting to solve the Schrödinger equation for the ground state of the hydrogen atom using the method of local moments. Except for special choices of $\phi_1(r)$, the basis functions generated by the Hamiltonian [cf. Eq. (3)] would have singularities at $r=0$ and would be inappropriate to represent $\exp(-r)$, the ground-state wavefunction for hydrogen. Consequently one would not expect the local moment method to be very useful for the hydrogen atom.

The local CI method permits a more appropriate choice of basis functions. We take

$$\phi_n(r) = r^n \exp(-\zeta r), \quad n = 0, 1, 2, \dots, N-1, \quad (5)$$

since

$$\exp(-r) = \sum_{n=0}^{\infty} \frac{(\zeta-1)^n}{n!} \phi_n(r). \quad (6)$$

The formula,

$$H\phi_n = (-\frac{1}{2}\nabla^2 - r^{-1})\phi_n \quad (7)$$

$$= -\frac{1}{2}\zeta^2\phi_n + [(n+1)\zeta-1]\phi_{n-1} - \frac{1}{2}n(n+1)\phi_{n-2}, \quad (8)$$

permits the recursive calculation of the $H^k\phi_n(r_0)$.

The results of solving Eq. (4) for the root closest to the exact value ($E_{\text{exact}} = -0.5$) for $\zeta = 0.9$ and 1.2, and for the local points $r_0 = 0.5, 2.0$, and 6.0, are presented in Table I. It is clear that the local CI method works, accurately reproducing the exact energy for varying choices of basis functions (i.e., the value of ζ)

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¹ H. J. Silverstone, M. L. Yin, and R. L. Somorjai, *J. Chem. Phys.* **47**, 4824 (1967).

² Also, cf. J. B. Delos and S. M. Blinder, *J. Chem. Phys.* **47**, 2784 (1967).

³ C. W. David and E. Eisler, *J. Chem. Phys.* **50**, 1477 (1969).

TABLE I. Local CI energy of hydrogen atom for various ζ and local points.^{a,b}

ζ	Number of basis functions N	Energy (a.u.) at local point r_0 (Bohr radii)		
		0.5	2.0	6.0
0.9	1	-0.6050000	-0.4550000	-0.4216666
	2	-0.4861089	-0.4965476	-0.4587604
	4	-0.4998897	-0.5000083	-0.4983472
	6	-0.4999992	-0.4999982	-0.4999953
	8	-0.4999999	-0.5000000	-0.4999999
	10		-0.5000000	-0.4999999
1.2	1	-0.3200000	-0.6200000	-0.6866666
	2	-0.4599405	-0.4199999	c
	4	-0.4992995	-0.5000199	c
	6	-0.4999774	-0.5000035	-0.4978747
	8	-0.4999996	-0.4999999	-0.4999932
	10		-0.5000000	-0.4999999

^a Basis is $[r^n \exp(-\zeta r) | n=1, 2, \dots, N]$.
^b $E_{\text{exact}} = -0.5$ a.u.

^c No real roots to local CI determinant found.

and for a wide range in the values of r_0 .

The hydrogen atom is perhaps too simple an example. A more substantial application of the local CI method is to H_2^+ .

HYDROGEN MOLECULE ION

The H_2^+ Schrödinger equation is separable in prolate spheroidal coordinates, and energies and wavefunctions have been obtained to high accuracy.⁴⁻⁷ We solve the Schrödinger equation (for an internuclear distance $R=2a_0$) both in its separated and unseparated forms and compare the results with those of more standard approaches.

Separated Equations

For σ states, the electronic Hamiltonian is⁴

$$H_{\text{elect}} = -\frac{2}{R^2} \frac{1}{\lambda^2 - \mu^2} \left[\frac{\partial}{\partial \lambda} (\lambda^2 - 1) \frac{\partial}{\partial \lambda} + 2R\lambda + \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial}{\partial \mu} \right]. \quad (9)$$

Write

$$\Psi(\lambda, \mu) = \Lambda(\lambda) M(\mu). \quad (10)$$

Then $\Lambda(\lambda)$ and $M(\mu)$ satisfy

$$H_\lambda \Lambda(\lambda) = [(\partial/\partial \lambda)(\lambda^2 - 1)(\partial/\partial \lambda) + 2R\lambda + \frac{1}{2}R^2 E \lambda^2] \Lambda(\lambda) \quad (11)$$

$$= -A \Lambda(\lambda), \quad (12)$$

$$H_\mu M(\mu) = [(\partial/\partial \mu)(1 - \mu^2)(\partial/\partial \mu) - \frac{1}{2}R^2 E \mu^2] M(\mu) \quad (13)$$

$$= A M(\mu). \quad (14)$$

We solve Eqs. (12) and (14) as eigenvalue equations for the separation constant A for $R=2a_0$. The E is varied as a parameter until both equations give the same A .

We use as basis functions for $\Lambda(\lambda)$,^{4b}

$$\Lambda_l^\sigma(\lambda) \equiv (\lambda + 1)^\sigma [(\lambda - 1)/(\lambda + 1)]^l \exp(-\rho \lambda), \quad (15)$$

$$\Lambda(\lambda) = \sum_{l=0}^{\infty} g_l \Lambda_l^\sigma(\lambda), \quad (16)$$

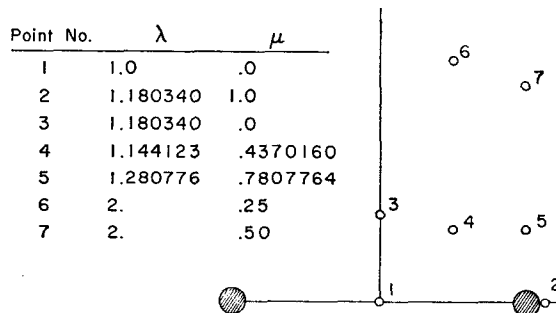


FIG. 1. The location of the points, with respect to the two protons, for which the local energies are evaluated.

⁴ (a) D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc. (London)* **A246**, 215 (1953); (b) G. Jaffe, *Z. Physik* **87**, 535 (1934); (c) E. A. Hylleraas, *ibid.* **71**, 739 (1931).
⁵ H. Wind, *J. Chem. Phys.* **42**, 2371 (1965).
⁶ J. M. Peek, *J. Chem. Phys.* **43**, 3004 (1965).
⁷ C. M. Rosenthal and E. B. Wilson, *Intern. J. Quantum Chem.* **2S**, 175 (1968).

TABLE II. Local CI energy (in a.u.) for H_2^+ from nonseparated and separated equations at various local points.^a

Local point No. ^b	λ	μ	$-E$ (nonseparated eq.) ^c	$-E$ (separated eqs.) ^d
1	1.0	0.0	1.1027	1.102634213
2	1.180340	1.0	1.1029	1.102634219
3	1.180340	0.0	1.1027	1.102634213
4	1.144123	0.4370160	1.1026	1.102634214
5	1.280776	0.7807764	1.1027	1.102634214
6	2.	0.25	1.1026	1.102634215
7	2.	0.5	1.1030	1.102634214

^a Internuclear distance, R , is $2a_0$. $E_{\text{exact}} = -1.1026342144949$ a.u. (Ref. 6).

^b Refers to point number on Figs. 1.

^c Basis of Eq. (21) with $(lm) = 01, 02, 03, 04, 05, 10, 11, 12$.

^d Basis of Eq. (15) (nine functions) and Eq. (19) (seven functions).

where

$$\rho \equiv (-R^2 E/2)^{1/2}, \quad (17)$$

$$\sigma \equiv -1 + (-2/E)^{1/2}. \quad (18)$$

Note that the basis functions Λ_l^σ are explicit functions of E . For $M(\mu)$, we use Legendre polynomials^{4c}:

$$M(\mu) = \sum_{n=0}^{\infty} f_n P_{2n}(\mu). \quad (19)$$

Calculation of $(H_\mu)^k P_{2m}(\mu)$ is greatly simplified by the recursion formula:

$$\begin{aligned} (H_\mu)^k P_{2m} &= (4m+1)^{-1} \rho^2 \\ &\times \{ [(2m+1)(2m+2)/(4m+3)] (H_\mu)^{k-1} P_{2m+2} \\ &+ [2m(2m-1)/(4m-1)] (H_\mu)^{k-1} P_{2m-2} \\ &+ [(2m+1)^2(4m+3)^{-1} + 4m^2(4m-1)^{-1} \\ &- \rho^{-2} 2m(2m+1)(4m+1)] (H_\mu)^{k-1} P_{2m} \}. \quad (20) \end{aligned}$$

A similar, more involved recursion formula for $(H_\lambda)^k \Lambda_l^\sigma$ is given in the Appendix.

The energies and coefficients for several local points are tabulated in Tables II and III. Figure 1 illustrates the location of these points with respect to the two protons. To obtain the exact energy accurate to nine significant figures at each local point, we used seven P_{2m} and nine Λ_l^σ .

Unseparated Equation

Since most molecular problems are not separable, it is instructive to solve H_2^+ without separating the λ and μ variables. Let the basis functions be

$$\phi_{lm}^\sigma(\lambda, \mu) \equiv \Lambda_l^\sigma(\lambda) P_{2m}(\mu), \quad (21)$$

$$\psi(\lambda, \mu) = \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} c_{lm} \phi_{lm}^\sigma(\lambda, \mu). \quad (22)$$

The straightforward computation of the $(H_{\text{elect}})^k \phi_{lm}^\sigma$ is complicated unfortunately by the factor $(\lambda^2 - \mu^2)^{-1}$

in H_{elect} . We found it more convenient to define an auxiliary Hamiltonian,

$$H_{\text{aux}} \equiv -\frac{1}{2} R^2 (\lambda^2 - \mu^2) (H_{\text{elect}} - E) \quad (23)$$

$$= H_\lambda + H_\mu. \quad (24)$$

An eigenfunction of H_{elect} with eigenvalue E is an eigenfunction of H_{aux} with eigenvalue zero, and vice versa. Equations (23) and (24) permit one to exploit

$$(H_{\text{aux}})^k \phi_{lm}^\sigma = \sum_{n=0}^k \binom{k}{n} [(H_\lambda)^n \Lambda_l^\sigma] [(H_\mu)^{k-n} P_{2m}]. \quad (25)$$

TABLE III. Coefficients for H_2^+ wavefunction at $R=2a_0$. $\psi = (\sum_l g_l \Lambda_l^\sigma) (\sum_m f_m P_{2m})$.

Coefficient	Exact ^a	Local CI ^b
g_0	1.	1.
g_1	0.0167800041	0.0167800036
g_2	0.000403899	0.000403900
g_3	0.0000351416	0.0000351407
g_4	0.000005147	0.000005151
g_5	0.000001016	0.000001007
g_6	0.000000245	0.000000251
g_7	0.000000068	0.000000069
g_8	0.000000021	0.000000023
f_0	1.145	1.145
f_1	0.298443002	0.298442999
f_2	0.011461687	0.011461688
f_3	0.0001836874	0.0001836876
f_4	0.0000016224	0.0000016225
f_5	0.0000000091	0.0000000087
f_6	0.35×10^{-10}	0.29×10^{-10}

^a Calculated from the known recurrence formulas for the coefficients using the energy and separation constant of Ref. 6.

^b Values at local point No. 4 of Fig. 1 ($\lambda = 1.144123$, $\mu = 0.4370160$).

To obtain E , first regard E as a parameter in H_{aux} and solve Eq. (4) for the eigenvalue of H_{aux} nearest zero. Then vary E until this eigenvalue becomes zero. Values of E so determined are listed in Table II, and the corresponding expansion coefficients c_{lm} are listed in Table IV. A total of nine basis functions were used.

Variational and Exact Wavefunctions

For comparison we have obtained the wavefunction (and energy, in the variational case) by the "standard" and variational methods. By "standard" method we mean take the exact energy and solve the well known recursion formulas⁸ for the coefficients, f_m and g_l . For the variational method, one diagonalizes the matrix of H_{elect} with respect to the ϕ_{lm}^σ . All the integrals can be evaluated using nothing more complicated than the incomplete gamma function, but we used instead a Gaussian quadrature.⁹ The variational and exact results are listed in Tables II-IV.

DISCUSSION

The local configuration interaction energies converged (cf. Tables II and V) towards the exact energy at each local point. The "rate of convergence" depended on both the local point and the selection of basis functions. Examination of the quantities $H^k\psi_{\text{exact}}(\mathbf{r}_0)$ for the exact ψ truncated at varying numbers of basis functions revealed a strong correlation between the accuracy of the truncated $H^k\psi_{\text{exact}}(\mathbf{r}_0)$ and the local CI energy. Moreover, the basis functions contributing strongly to $H^k\psi_{\text{exact}}(\mathbf{r}_0)$ were not independent of \mathbf{r}_0 and not always the ones contribut-

TABLE IV. Coefficients for H_2^+ wavefunction at $R=2a_0$.
 $\psi = \sum_{l,m} c_{lm} \phi_{lm}^\sigma$.

Coefficient	Exact values ^a	Variational	Local CI ^b
c_{00}	1.145	1.145	1.145
c_{01}	0.298443002	0.298443002	0.2986
c_{02}	0.011461687	0.011461695	0.011463
c_{03}	0.0001837	0.0001841	0.0001835
c_{04}	0.000001622	0.000001626	0.000001629
c_{05}	0.0000000091	0.0000000091	0.0000000064
c_{10}	0.0192	0.0194	0.0190
c_{11}	0.00501	0.00506	0.0048
c_{12}	0.000192	0.000194	0.00022

^a Calculated from the known recurrence formulas for the coefficients using the energy and separation constant of Ref. 7.

^b Computed from $(H_{\text{aux}})^k \psi = 0$, $k=1, \dots, 9$, at local point No. 4 of Fig. 1 ($\lambda=1.144123$, $\mu=0.4370160$).

⁸ See, e.g., Ref. 5.

⁹ A. D. McLean and M. Yoshimine, IBM J. Res. Develop. 9, 203 (1965).

TABLE V. Convergence of local CI energy and variational energy for H_2^+ .^a

No. functions	$-E_{\text{MCLI}}^{\text{b,c}}$	$-E_{\text{var}}^{\text{b}}$
4	1.1031	1.102627
5	1.1029	1.102627
6	1.1029	1.102627
7	1.10268	1.1026340
8	1.102637	1.1026342140
9	1.102637	1.1026342143

^a $E_{\text{exact}} = -1.1026342144949$ (Ref. 6).

^b Basis is $\{\phi_{00}^\sigma, \phi_{01}^\sigma, \dots, \phi_{05}^\sigma, \phi_{10}^\sigma, \phi_{11}^\sigma, \phi_{12}^\sigma\}$ and functions are taken in the order given.

^c Local point $\lambda=1.144123$, $\mu=0.437016$. (Point No. 4 of Fig. 1.)

ing most strongly to the variational energy. The nine basis functions used in calculating the local CI energies in Column 4 of Table II gave the variational energy to 11 significant figures. The poorer of the local CI values, however, were found to improve with a different selection of basis functions chosen to make the truncated $H^k\psi_{\text{exact}}(\mathbf{r}_0)$ more accurate.

The accuracy obtained solving the separated equations was better than nine significant figures. Solving the unseparated equation gave five significant figures. The separated-equation basis corresponds to 63 product-type basis functions versus the nine used in the unseparated calculation, which explains the difference in accuracy. A main point of the nine-basis-function calculation was to compare the local CI accuracy (five significant figures) to the variational principle accuracy (11 significant figures) with the same basis. Note that although the corresponding wavefunctions are of comparable accuracy (Table IV), the error in the variational energy is much smaller (second order, because of the variational principle) than the error in the local CI energy.

No perverse numerical difficulties were encountered, but to minimize roundoff error the determinants had to be evaluated carefully.¹⁰

CONCLUSION

The applicability of the local configuration interaction method has been demonstrated for electronic systems. The rate of convergence of the method is slower than that of the variational method and depends more sensitively on the choice of basis functions. Because of the slow convergence of the energy, it would be advisable not to use the local CI method when the integrals required for a variational calculation can be easily evaluated. The possible usefulness of

¹⁰ J. Pfann and J. Straka, Commun. Assoc. Computing Machinery 8, 668 (1965), Algorithm 269.

the local CI method is for those cases for which the integrals can not be easily evaluated.

APPENDIX: RECURSION FORMULA FOR $(H_\lambda)^k \Lambda l^\sigma$

Using the definition of $\Lambda l^\sigma(\lambda)$ [Eq. (15)], one can easily show that

$$\lambda \Lambda l^\sigma = \frac{1}{2}(\Lambda l^{\sigma+1} + \Lambda l_{l+1}^{\sigma+1}), \quad (\text{A1})$$

$$\Lambda l^\sigma = \frac{1}{2}(\Lambda l^{\sigma+1} - \Lambda l_{l+1}^{\sigma+1}), \quad (\text{A2})$$

and

$$(d/d\lambda) \Lambda l^\sigma = \sigma \Lambda l^{\sigma-1} - p \Lambda l^\sigma + l \Lambda_{l-1}^{\sigma-1} - l \Lambda l^{\sigma-1}. \quad (\text{A3})$$

Then H_λ [Eq. (11)] on Λl^σ gives

$$H_\lambda \Lambda l^\sigma = \sum_{n=-1}^3 d_n l^\sigma \Lambda l_{l+n}^{\sigma+2}, \quad (\text{A4})$$

where

$$d_{-1} l^\sigma = \frac{1}{4} l^2, \quad (\text{A5})$$

$$d_0 l^\sigma = -l^2 - (l + \frac{1}{2})(p - \frac{1}{2}\sigma) - \frac{1}{4}(p^2 - 2R), \quad (\text{A6})$$

$$d_1 l^\sigma = \{3l^2 - 3l\sigma + 4lp - \sigma + \frac{1}{2}\sigma^2 + p^2 - 2p\sigma\}/2, \quad (\text{A7})$$

$$d_2 l^\sigma = -l^2 - lp + (3l\sigma/2) + p\sigma - \frac{1}{4}(2R + p^2 - \sigma - 2p + 2\sigma^2), \quad (\text{A8})$$

$$d_3 l^\sigma = \frac{1}{4}(l - \sigma)^2. \quad (\text{A9})$$

Multiplication of Eq. (A4) by H_λ^{k-1} then yields the recursion formula,

$$(H_\lambda)^k \Lambda l^\sigma = \sum_{n=-1}^3 d_n l^\sigma (H_\lambda)^{k-1} \Lambda l_{l+n}^{\sigma+2}. \quad (\text{A10})$$

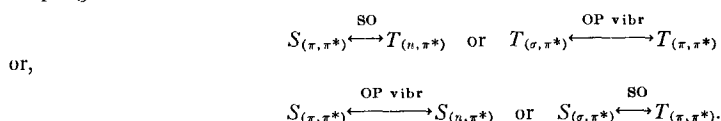
Vibronic Spin-Orbit Interaction in the Phosphorescence Spectrum of Phenazine*

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The polarization of the phosphorescence spectrum (PS) of phenazine in 3-methylpentane and EPA as solvents was measured. If the strong 0,0 band, which was negative polarized, is disregarded, the other bands are found about equally positive and negative polarized. This indicates the presence of a rather strong in-plane component of the emitting oscillator. The Raman and infrared spectra and a sharp PS of phenazine in *n*-heptane as a solvent were recorded. A vibrational analysis of these spectra was performed and the results compared with the polarization of the PS of phenazine in 3-methylpentane and EPA. All negative-polarized lines of the PS could be assigned to Raman frequencies and all positive-polarized lines to infrared modes. The presence of the positive-polarized lines (out-of-plane modes) of appreciable intensity indicated rather strong vibronic spin-orbit (SO) coupling (second-order perturbations) in phenazine. The possible coupling schemes could be:



Both coupling schemes involve out-of-plane vibrations (OP vibr).

I. INTRODUCTION

The transition $T_1 \rightarrow S_0$ is forbidden by the selection rule $\Delta S = 0$. However, in deriving this selection rule the following assumptions are made:

- (1) The nuclear and electronic motions in a molecule are independent.
- (2) The spin and orbital motions of an electron are independent.

These assumptions, however, are not entirely correct: if an electron changes its spin direction because of

spin-orbit interaction (first-order perturbations), the transition $T_1 \rightarrow S_0$ will occur to a certain degree, and the resulting emission is called phosphorescence.¹

In addition to spin-orbit interaction, second-order perturbations can also be important and be evident in three forms²:

- (1) Direct vibronic spin-orbit coupling.
- (2) Vibronic coupling of T_1 with an intermediate T -state spin-orbit coupled to a perturbing S state.

* This investigation was conducted by the NELC Microelectronics Laboratory under the sponsorship of the Director of Naval Laboratories. Presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, September 1968.

¹ For a review of the "triplet state" see S. K. Lower and M. A. El-Sayed, *Chem. Rev.* **66**, 199 (1966). This article contains a collection of the most important papers on the subject up to mid 1965.

² A. C. Albrecht, *J. Chem. Phys.* **38**, 354 (1963). This paper also contains older references on the subject.