

Accurate ground-state calculations of H_2^+ using basis sets of atom-centered Slater-type orbitals

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(Received 24 September 1992)

The variational method is used to find the ground-state energy of the molecular hydrogen ion, H_2^+ , by employing a linear combination of atomic orbitals (LCAO) of the Slater type, all with the same exponential parameter ζ . For the equilibrium position, $R = 2$ a.u., eight-digit accuracy was achieved using 21 orbitals on each nucleus, with the highest principal quantum number, $N = 6$. Beyond $R = 50$, thirteen-digit accuracy is obtained. The wave function is given for various LCAO at the equilibrium position. Strategies developed here will be useful in our studies of polyatomic nonlinear molecules.

PACS number(s): 31.20.Di

INTRODUCTION

Basis-set methods, i.e., the algebraic approximation method, in molecular electronic structure calculations have been shown by Wells and Wilson [1] to give excellent results for simple molecules, including H_2^+ . They employed an even-tempered basis set of Gaussian-type orbitals (GTO's). In this paper, we use the more "intractable" [2] Slater-type orbitals (STO's) as basis with the hope of developing strategies so that we will be able to take advantage of their more physical nature for use in scattering phenomena and molecular structure calculations. Wells and Wilson also emphasize the advantages of basis-set methods over methods employing numerical grids, especially in regard to nonlinear polyatomic molecules.

Bishop and Schneider [3], in their study of transforms, remarked that completeness in basis sets for s orbitals may be achieved by variation of the principal quantum number or the exponential parameter. Thinking of the first possibility, Jones, Etemadi, and Brown [4] used s orbitals from $1s$ to $8s$ to obtain convergence with these spherically symmetric orbitals on the nuclei of H_2^+ . Encouraged by these results, we extend our study by use of an ordered sequence of orbitals with increasing principal quantum numbers and angular momentum. (All orbitals have the same orbital parameter or screening constant ζ .) By this procedure, the ground-state energy of H_2^+ for nuclear separations from 0.2 to 50 a.u. is calculated to an accuracy of from six to thirteen digits. In addition, the wave function for the equilibrium position ($R = 2.0$ a.u.) is given for various numbers of orbitals.

Finkelstein and Horowitz [5] were the first to use $1s$ orbitals on each nucleus with an adjustable orbital exponent. Dickinson [6] (corrected by Geller and Frost [7]) used $1s$ and $2p$ on each nucleus. Miller and Lykos [8] used a $1s$, $2p$, and $3d$ orbital on each nucleus. (We note that our result for a $1s$, $2s$, and $2p$ orbital on each nucleus is more accurate.)

LCAO METHOD FOR H_2^+

In the variational treatment of a quantum-mechanical system, the ψ function with one or more adjustable constants or parameters is assumed as the solution of the problem, and then the parameters are adjusted to minimize the energy. For our specific example, we take a linear combination of atomic orbitals (LCAO), all with the same value for the nonlinear parameter ζ , for our ψ function. A STO has the form

$$\chi = A r^{N-1} e^{-\zeta r} Y_L^M(\theta, \varphi), \quad A = \left[\frac{(2\zeta)^{2N+1}}{(2N)!} \right]^{1/2}.$$

We take a straightforward linear combination of STO's,

$$\psi = K \sum_{N=1}^{N_{\text{high}}} \sum_{L=0}^{N-1} C_{NL} A_N r^{N-1} e^{-\zeta r} Y_L^0(\theta, \varphi),$$

as our LCAO for the ground state ($M = 0$) and center a set on each nucleus, i.e., nucleus a and b . K is the normalization constant chosen such that

$$\int \Psi^* \Psi d\tau = 1 \quad (\Psi = \psi_a + \psi_b).$$

TABLE I. Exponential parameter ζ at the lowest energy for various values of the internuclear distance R and maximum principal quantum number N_{high} for a LCAO, pertaining to H_2^+ .

| R | N_{high} | | | | | |
|------|-------------------|------|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| 0.2 | 1.94 | 2.12 | 2.50 | 2.50 | | |
| 1.0 | 1.54 | 1.91 | 1.93 | 2.11 | 2.20 | 2.30 |
| 2.0 | 1.24 | 1.58 | 1.70 | 1.76 | 1.93 | 2.00 |
| 3.0 | 1.09 | 1.34 | 1.56 | 1.57 | 1.68 | 1.80 |
| 20.0 | 1.00 | 0.98 | 0.98 | 0.97 | 1.00 | 1.00 |
| 50.0 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

C_{NL} are the linear parameters and N_{high} is the value of the largest principal quantum number used for a given trial (it will vary from 1 to 6).

We write the Schrödinger equation

$$H\Psi = E\Psi$$

and substitute in the Ψ under consideration, and arrive at a secular equation for the energy (eigenvalue) [9]. This eigenvalue problem was solved on a CRAY-YMP computer using an IMSL program. The matrix elements for this problem can essentially be written as combinations of overlap integrals [10]. Tai [11] pointed out numerous errors in early work that evaluated overlap integrals. It is only recently that reliable methods for the evaluation of STO overlap integrals with high quantum numbers have been developed (see Weniger and Steinborn [12], and Jones [13]).

RESULTS

Table I shows the values for ζ that give the minimum energy for various values of the internuclear distance and N_{high} . Table II shows the corresponding electronic energies. The exact energy for the first row was taken from Wind [14]. The other exact energies were taken from Madsen and Peek [15]. (The values were obtained by subtracting the Coulomb energy, $1/R$, of the nuclei from the electronic energies.) Using $N_{\text{high}}=6$, which puts 21 orbitals on each nucleus, and $R=2$, we obtain the same energy to the eight digits given by Wells and Wilson [1] who used 42 Gaussian-type orbitals on each nucleus. The faster convergence of STO's was expected. For the large separation of nuclei at $R=50$, we obtain full thirteen-digit agreement with Madsen and Peek, for $N_{\text{high}}=5$, i.e., 15 orbitals on each nuclei. This complete agreement is found for all values of R beyond 50. At $R=0.2$, we can only use ten orbitals ($N_{\text{high}}=4$), otherwise, linear dependencies prevent the IMSL program from functioning. Nevertheless, even at the small distance of $R=0.2$, practically six-digit accuracy is achieved. Table III records the orbital coefficients obtained from the eigenvectors of the energy minima at the equilibrium distance, $R=2$ a.u., for a various number of orbitals determined by N_{high} .

CONCLUSION

We have shown that STO's are a viable alternative to GTO's when dealing with a simple one-electron molecule. Furthermore, it has been demonstrated that orbitals with varying principal quantum numbers are an effective replacement for even-tempered basis sets that mostly vary the nonlinear orbital parameters. The Löwdin α -function method [16] has proven to be effective in a production mode for generating accurate values of overlap integrals. More complicated molecules are under investigation using these methods.

TABLE II. The electronic energy of H_2^+ for various internuclear distances R and for LCAO with highest quantum number N_{high} .

| R | $N_{\text{high}}=1$ | $N_{\text{high}}=2$ | $N_{\text{high}}=3$ | $N_{\text{high}}=4$ | $N_{\text{high}}=5$ | $N_{\text{high}}=6$ | Exact |
|------|---------------------|---------------------|---------------------|----------------------|----------------------|----------------------|----------------------|
| 0.2 | -1.928 325 | -1.928 5351 2 | -1.928 609 7 | -1.928 609 7 | Unstable | Unstable | -1.928 620 2 |
| 1.0 | -1.440 996 18 | -1.451 530 400 2 | -1.451 700 809 | -1.451 780 299 | -1.451 784 39 | -1.451 785 79 | -1.451 786 313 378 1 |
| 2.0 | -1.085 050 16 | -1.102 184 971 | -1.102 579 075 | -1.102 642 5 | -1.102 633 47 | -1.102 634 0 | -1.102 634 214 494 9 |
| 3.0 | -0.897 767 | -0.909 963 8 | -0.910 855 10 | -0.910 888 78 | -0.918 954 4 | -0.910 896 08 | -0.910 896 197 382 3 |
| 20.0 | -0.550 000 03 | -0.550 012 7 | -0.550 014 240 | -0.550 014 258 8 | -0.550 014 259 29 | -0.550 014 259 327 | -0.550 014 259 330 9 |
| 50.0 | -0.520 000 00 | -0.520 000 32 | -0.520 000 360 50 | -0.520 000 360 551 6 | -0.520 000 360 551 8 | -0.520 000 360 551 8 | -0.520 000 360 551 8 |

TABLE III. Coefficients C_{NL} before orbitals that make up LCAO with highest quantum number N_{high} , at the equilibrium distance $R = 2.0$ a.u., for H_2^+ . Each nucleus has identical orbitals. K is the normalization constant.

| Orbital | $N_{\text{high}} = 2$ | $N_{\text{high}} = 3$ | $N_{\text{high}} = 4$ | $N_{\text{high}} = 5$ | $N_{\text{high}} = 6$ |
|-------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| 1s | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 2s | 0.597 502 | 0.598 182 | 0.636 512 | 0.737 380 | 0.745 909 |
| 2p σ | 0.185 418 | 0.130 488 | 0.112 303 | 0.094 421 | 0.094 957 |
| 3s | | 0.191 573 | 0.209 123 | 0.448 071 | 0.400 324 |
| 3p σ | | 0.112 262 | 0.150 186 | 0.152 873 | 0.153 366 |
| 3d σ | | 0.045 904 | 0.047 706 | 0.026 401 | 0.026 356 |
| 4s | | | 0.060 503 | 0.076 795 | 0.164 076 |
| 4p σ | | | 0.013 549 | 0.069 072 | 0.076 866 |
| 4d σ | | | 0.013 046 | 0.051 045 | 0.053 648 |
| 4f σ | | | 0.013 812 | 0.016 356 | 0.016 315 |
| 5s | | | | 0.111 965 | 0.031 038 |
| 5p σ | | | | 0.019 395 | 0.023 338 |
| 5d σ | | | | -0.005 287 | -0.000 982 |
| 5f σ | | | | 0.000 791 | 0.004 847 |
| 5g σ | | | | 0.003 948 | 0.007 663 |
| 6s | | | | | 0.035 435 1 |
| 6p σ | | | | | 0.006 673 |
| 6d σ | | | | | 0.003 870 |
| 6f σ | | | | | -0.000 462 |
| 6g σ | | | | | -0.002 835 |
| 6h σ | | | | | 0.001 134 |
| K | 0.131 681 | 0.105 231 | 0.093 314 4 | 0.063 955 1 | 0.063 350 8 |

ACKNOWLEDGMENTS

Support for this work was provided by the Air Force Office of Scientific Research under Contract No. F49620-92-J-0063, and NASA (CeNNas). The authors thank the Florida State University Supercomputer Computations Research Institute for computer time.

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