ELECTRON ATTRACTION AS A MECHANISM FOR THE CHEMICAL
BOND OF GROUND STATE H_2 *

by

Donald Greenspan
Mathematics Department
University of Texas at Arlington

TR #294

ABSTRACT

Previously, electron attraction, incorporated into classical models of the chemical bond, yielded correct bond lengths and vibrational frequencies for all the diatomic molecules through O_2 . In each case, maximally symmetric electron-nuclei configurations were utilized. In this paper, which concentrates only on ground state H_2 , it is shown that maximal symmetry is not necessary for the attainment of correct results.

---

* Calculations performed on the Cray YMP at the University of Texas Center for High Performance Computation

1. Introduction. Theoretical work has shown that pairs of electrons need not always repel^(1,2). Nobelist John Bardeen and his associates showed, for example, that the quantum mechanical theory for superconductivity requires electron attraction⁽¹⁾. This is not inconsistent with the recent work on electron substructure by Nobelist H. G. Dehmelt^(3,4). Motivated by these current ideas, we have been exploring the possibility that the chemical bond is the result of electron attraction. The resulting models are semiclassical in the sense that they incorporate a nonstandard force into Newtonian dynamical equations. We have shown⁽⁵⁻⁷⁾ that classical dynamical simulation with paired electron attractions yields the correct bond lengths and vibrational frequencies for the diatomic molecules H_2^1 , H_2^2 , H_2^3 , H^1H^2 , H^1H^3 , Li_2^7 , B_2^{11} , C_2^{11} , N_2^{14} , O_2^{16} , Li^7H^1 and Li^7H^2 . In each case, a maximum of symmetry was incorporated into the calculations. In this paper, by concentrating only on ground state H_2 , we will show that a maximum of symmetry is not necessary to approximate correctly the experimental bond length and experimental vibrational frequency, which are, respectively, 0.742 Å and $(1.318)10^{14} \text{ H}^{(8,9)}$.

2. Mathematical Preliminaries. Note first that the energy E of ground state H_2 is⁽¹⁰⁾

$$(2.1) \quad E = -(50.7289)10^{-12} \text{ erg.}$$

Next, let us denote the electrons by P_1 and P_3 , while the protons are denoted by P_2 and P_4 . Assume for the moment that the only forces are coulombic. In cgs units, for $i=1,2,3,4$, and at any time t , let P_i be located at $\vec{r}_i = (x_i, y_i, z_i)$, have velocity $\vec{v}_i = (\dot{x}_i, \dot{y}_i, \dot{z}_i)$, and have acceleration $\vec{a}_i = (\ddot{x}_i, \ddot{y}_i, \ddot{z}_i)$. Then the classical equations of motion for the P_i are

$$(2.2) \quad m_i \vec{a}_i = \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{e_i e_j}{r_{ij}^2} \frac{\vec{r}_{ji}}{r_{ij}}, \quad i=1,2,3,4,$$

in which $\vec{r}_{ji}$ is the vector from P_j to P_i , $r_{ij} = \|\vec{r}_{ij}\|$, and

$$(2.3) \quad e_1 = e_3 = -e_2 = -e_4 = (-4.8028) 10^{-10} \text{ esu},$$

$$(2.4) \quad m_1 = m_3 = (9.1085) 10^{-28} \text{ g},$$

$$(2.5) \quad m_2 = m_4 = (16724) 10^{-28} \text{ g}.$$

We assume now that P_1 and P_3 attract, rather than repel. For computational convenience, we also set $\vec{R}_i = (X_i, Y_i, Z_i)$ and make the transformations

$$(2.6) \quad \vec{R}_i = 10^{12} \vec{r}_i$$

$$(2.7) \quad T = 10^{22} t.$$

Then system (2.2) transforms into the following system:

$$(2.8) \quad \frac{d^2 X_1}{dT^2} = (2.5324576) \left(-\frac{X_1 - X_2}{R_{12}^3} - \frac{X_1 - X_3}{R_{13}^3} - \frac{X_1 - X_4}{R_{14}^3} \right)$$

$$(2.9) \quad \frac{d^2 Y_1}{dT^2} = (2.5324576) \left(-\frac{Y_1 - Y_2}{R_{12}^3} - \frac{Y_1 - Y_3}{R_{13}^3} - \frac{Y_1 - Y_4}{R_{14}^3} \right)$$

$$(2.10) \quad \frac{d^2 Z_1}{dT^2} = (2.5324576) \left(-\frac{Z_1 - Z_2}{R_{12}^3} - \frac{Z_1 - Z_3}{R_{13}^3} - \frac{Z_1 - Z_4}{R_{14}^3} \right)$$

$$(2.11) \quad \frac{d^2 X_2}{dT^2} = (1.379269) 10^{-3} \left(-\frac{X_2 - X_1}{R_{12}^3} - \frac{X_2 - X_3}{R_{23}^3} + \frac{X_2 - X_4}{R_{24}^3} \right)$$

$$(2.12) \quad \frac{d^2 Y_2}{dT^2} = (1.379269) 10^{-3} \left(-\frac{Y_2 - Y_1}{R_{12}^3} - \frac{Y_2 - Y_3}{R_{23}^3} + \frac{Y_2 - Y_4}{R_{24}^3} \right)$$

$$(2.13) \quad \frac{d^2 Z_2}{dT^2} = (1.379269) 10^{-3} \left(-\frac{Z_2 - Z_1}{R_{12}^3} - \frac{Z_2 - Z_3}{R_{23}^3} + \frac{Z_2 - Z_4}{R_{24}^3} \right)$$

$$(2.14) \quad \frac{d^2 X_3}{dT^2} = 2.5324576 \left(-\frac{X_3 - X_1}{R_{13}^3} - \frac{X_3 - X_2}{R_{23}^3} - \frac{X_3 - X_4}{R_{34}^3} \right)$$

$$(2.15) \quad \frac{d^2 Y_3}{dT^2} = 2.5324576 \left(-\frac{Y_3 - Y_1}{R_{13}^3} - \frac{Y_3 - Y_2}{R_{23}^3} - \frac{Y_3 - Y_4}{R_{34}^3} \right)$$

$$(2.16) \quad \frac{d^2 Z_3}{dT^2} = 2.5324576 \left(-\frac{Z_3 - Z_1}{R_{13}^3} - \frac{Z_3 - Z_2}{R_{23}^3} - \frac{Z_3 - Z_4}{R_{34}^3} \right)$$

$$(2.17) \quad \frac{d^2 X_4}{dT^2} = (1.379269)10^{-3} \left(-\frac{X_4 - X_1}{R_{14}^3} + \frac{X_4 - X_2}{R_{24}^3} - \frac{X_4 - X_3}{R_{34}^3} \right)$$

$$(2.18) \quad \frac{d^2 Y_4}{dT^2} = (1.379269)10^{-3} \left(-\frac{Y_4 - Y_1}{R_{14}^3} + \frac{Y_4 - Y_2}{R_{24}^3} - \frac{Y_4 - Y_3}{R_{34}^3} \right)$$

$$(2.19) \quad \frac{d^2 Z_4}{dT^2} = (1.379269)10^{-3} \left(-\frac{Z_4 - Z_1}{R_{14}^3} + \frac{Z_4 - Z_2}{R_{24}^3} - \frac{Z_4 - Z_3}{R_{34}^3} \right)$$

It is system (2.8)-(2.19) which we will solve numerically from arbitrarily selected initial data. However, conservation of energy is essential in the numerical procedure, so that we must and will utilize numerical methodology designed for just such a purpose (11).

Note that for convenience we set

$$\vec{V}_i = \left(\frac{dX_i}{dT}, \frac{dY_i}{dT}, \frac{dZ_i}{dT} \right)$$

and observe that

$$\vec{v}_i = 10^{10} \vec{V}_i.$$

Finally, observe that the total energy E of the system is given by

$$(2.20) \quad E = \frac{1}{2}(9.1085)10^{-28}(v_1^2 + v_3^2) + \frac{1}{2}(16724)10^{-28}(v_2^2 + v_4^2) \\ + (23.06689)10^{-20}(-1/r_{12} - 1/r_{13} - 1/r_{14} - 1/r_{23} + 1/r_{24} - 1/r_{34}) ,$$

or, equivalently, by

$$(2.21) \quad E = \frac{1}{2}(9.1085)10^{-8}(V_1^2 + V_3^2) + \frac{1}{2}(16724)10^{-8}(V_2^2 + V_4^2) \\ + (23.06689)10^{-8}(-1/R_{12} - 1/R_{13} - 1/R_{14} - 1/R_{23} + 1/R_{24} - 1/R_{34}) .$$

3. Maximally Symmetric Systems. In setting initial data for computer calculations, we first incorporate as much symmetry as possible and repeat, but with increased accuracy, calculations reported previously⁽⁵⁾. Thus, we set P_1 at $(0,0,Z)$, P_2 at $(X,0,0)$, P_3 at $(0,0,-Z)$, and P_4 at $(-X,0,0)$. The velocities of P_2 and P_4 are taken to be zero, initially, while the velocities of P_1 and P_3 are taken to be $(0,VY,0)$ and $(0,-VY,0)$, respectively. The value VY will be determined from (2.1) and (2.21) after all other initial data are given. Calculations were made with several choices of ΔT to assure accuracy. The results to be reported are for $\Delta T = 2.0$. The implicit convergence tolerance for position was 10^{-6} , while that for velocity was 10^{-13} . Simulations were executed for 40,000,000 time steps. The energy was conserved throughout each calculation. A typical vector computer program is available¹² for the interested reader. The results are given in Table I.

Since the average experimental frequency f is $(1.318)10^{14}$ H and the average experimental molecular diameter d is $0.742 \text{ \AA}$, it is then seen readily that all the results in Table I are in good agreement with experiment. This is unexpected because the choices of initial data may be inconsistent in that, for each given set of initial positions, the velocities of P_2 and P_4 need not necessarily be

equal to zero. Moreover, though initial data can be contrived readily to yield f or d to within acceptable bounds, initial data cannot be chosen to assure, a priori, the correctness of both f and d.

TABLE I

	X	Z	VY	f (10^{14} H)	d ($\text{\AA}$)
1	4000	4500	0.033020594	1.366	0.776
2	4000	4200	0.034271092	1.375	0.770
3	4000	4000	0.035125168	1.383	0.764
4	3800	5000	0.031242354	1.377	0.794
5	4435	5000	0.030437537	1.363	0.790
6	3000	4360	0.035006180	1.339	0.808
7	4000	10000	0.013916043	1.409	0.762

4. Partially Symmetric Systems. In Section 3, all systems considered yielded two dimensional motion for P_1 and P_3 in the YZ plane, symmetrically about the origin, and yielded one dimensional motion for P_2 and P_4 along the X axis, symmetrically about the origin. In this section we consider sets of initial data which yield fully three dimensional motions under a modicum of symmetry. In all the cases to be considered the initial values of Y_1 , Y_2 , Z_2 , Y_3 , Y_4 , and Z_4 are zero. Thus, the electrons and the protons, initially, are in the XZ plane. The initial velocity vectors of P_2 and P_4 are taken to be zero. The initial velocity vector for P_1 is $(0, VY, 0)$ and that for P_3 is $(0, -VY, 0)$. The remaining initial positions are given in Table II. The value VY in the table was determined from (2.1) and (2.21). The time step was $\Delta T = 2.0$ and the results were checked periodically with $\Delta T = 0.2$. The tabular selections were motivated by the better results in Table I. Each case was run for a minimum of 40,000,000 time steps.

TABLE II

	X_1	Z_1	X_2	X_3	Z_3	X_4	VY	$d(\text{\AA})$	$f(10^{14}\text{H})$
1	1000	5000	4200	1000	-5000	-4200	0.03082428	0.7984	1.351
2	1000	4000	4200	1000	-4000	-4200	0.03491311	0.7721	1.374
3	1000	5000	3800	1000	-5000	-3800	0.03126779	0.8051	1.334
4	1000	3600	3800	1000	-3600	-3800	0.03763350	0.7662	1.362
5	1000	3800	3600	1000	-3800	-3600	0.03706020	0.7795	1.319
6	2000	5000	4200	2000	-5000	-4200	0.03095034	0.8275	1.278
7	1000	5000	3400	1000	-5000	-3400	0.03158437	0.8184	1.322
8	500	3600	3800	-500	-3600	-3800	0.03739651	0.7553	1.412
9	500	3800	3600	-500	-3800	-3600	0.03688544	0.7665	1.392
10	500	4000	4000	-500	-4000	-4000	0.03513952	0.7663	1.393

In each case in Table II, electron motion could be characterized as follows. The motion of P_1 , for example, was that of oscillation from a position near P_2 to a position near P_4 and then back and forth again. All the tabular results are considered to be good. The results of Case 4 are particularly good in that both the frequency and the diameter differ from the experimental results by 3%. In Case 5, the diameter is in error by 5%, but the frequency is in error by only 0.08%. Case 6 shows a relatively large diameter but a compensating decrease in frequency. For Table II, the average diameter is $0.7855 \text{ \AA}$ and the average frequency is $(1.354)10^{14} \text{ H}$, which are in error by 5.8% and 2.7%, respectively.

5. Nonsymmetric Systems. Our initial approach to nonsymmetric systems was as follows. The protons were set on the X axis initially with $3000 \leq X_2 \leq 7000$ and with $X_4 = -X_2$. Pairs of typical nonsymmetric initial positions for P_1 and P_3 were, for example,

- (a) (1,0,4000), (0,0,-4000)
- (b) (1000,0,3800), (0,0,-3800)
- (c) (5000,0,4000), (0,0,-2500)
- (d) (3500,0,2000), (-6000,0,-3500) .

The initial velocities for P_2 and P_4 were zero, while those for P_1 and P_3 were $(0, VY, 0)$, $(0, -VY, 0)$, respectively. The constant VY was determined from (2.1) and (2.21). A variable time step was implemented as follows. For $i=1,2,3,4$; $j=1,2,3,4$,

$$\begin{aligned} \Delta T &= 2.0 && \text{if } \min |P_i P_j| > 3000 \\ \Delta T &= 0.2 && \text{if } \min |P_i P_j| < 3000 \\ \Delta T &= 0.02 && \text{if } \min |P_i P_j| < 2000 \\ \Delta T &= 0.002 && \text{if } \min |P_i P_j| < 1000 \\ \Delta T &= 0.0002 && \text{if } \min |P_i P_j| < 500. \end{aligned}$$

In all, 74 cases were run. In 72 of these, P_1 and P_3 , in time, orbited each other in a close orbit whose diameter was smaller than 1000 units. In six of these cases, one of P_1 or P_3 was "sling shotted" outward with a sufficiently high velocity which made the time steps in use suspect. The resulting nonperiodic motions, the need for small time steps, and the very large variety of possible initial data made the choice of a reasonable sample and of computer implementation unfeasible at the present time. The following simplistic approach, first recommended by Gillespie⁽¹³⁾, was therefore implemented.

The closely orbiting electron pair phenomenon was simulated by combining P_1 and P_3 into a single particle of charge and mass twice that of a single electron. The new particle was denoted by P_1 and the protons were now denoted by P_2 and P_3 . Initially, P_2 was set at $(X_2, 0, 0)$ and P_3 at $(-X_2, 0, 0)$ with zero velocities. P_1 was set at $(X_1, 0, Z_1)$ with velocity $(0, VY, 0)$. The value VY was determined from the energy equation

$$-(50.7289)10^{-4} = \frac{1}{2}(18.2170)(VY)^2$$

$$+23.06689(-2/R_{12}-2/R_{13}+1/R_{23})$$

Selected computer results are recorded in Table III. In each case the time step was $\Delta T=2.0$. The vibrational motions were larger than those which resulted in previous sections. The average diameter and average frequency of the tabulated results are $0.7399 \text{ \AA}$ and $(1.592)10^{14} \text{ H}$, respectively. Considering the simplicity of the model, the results recorded in the table are deemed to be of sufficient accuracy to warrant the more precise, full, four-body study using relatively small time steps.

TABLE III

	x_1	z_1	x_2	x_3	VY	$d(\text{\AA})$	$f(10^{14} \text{ H})$
1	0	7000	5500	-5500	0.018727837	0.7384	1.634
2	0	7000	6000	-6000	0.018186690	0.7637	1.613
3	500	6000	4500	-4500	0.022639535	0.6984	1.667
4	500	7000	5000	-5000	0.019167789	0.7258	1.603
5	500	6000	6000	-6000	0.020660680	0.8300	1.408
6	1000	4000	4500	-4500	0.029315004	0.6830	1.629

References

1. J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev., 108, 1957, p 1175.
2. W. M. Honig, D. W. Kraft, and E. Panarella, QUANTUM UNCERTAINTIES, Plenum, N.Y., 1987, pp 147, 151.
3. H. Dehmelt, Proc. Nat. Acad. Sci. USA, 86, 1989, p 8618.
4. R. F. O'Connell, Found. Phys., 23, 1993, p 461.
5. D. Greenspan, Mol. Phys., 74, 1991, p 1015.
6. D. Greenspan, Phys. Essays, 5, 1992, p 554.
7. D. Greenspan, Comp. Math. Applic., 25, 1993, p 75.
8. L. Pauling, THE NATURE OF THE CHEMICAL BOND, Cornell Univ. Press, Ithaca, 1973.
9. B. H. Mahan, UNIVERSITY CHEMISTRY, Addison-Wesley, Reading, MA, 1966.
10. G. Herzberg, MOLECULAR SPECTRA AND MOLECULAR STRUCTURE, van Nostrand, N.Y., 1965, p 532.
11. D. Greenspan, ARITHMETIC APPLIED MATHEMATICS, Pergamon, Oxford, 1980, pp 20-30.
12. D. Greenspan, TR #278, Math. Dept., Univ. Texas at Arlington, 1991.
13. R. J. Gillespie, J. Chem. Ed., 40, 1963, p 295.