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**DYNAMICAL GENERATION OF ELECTRON MOTIONS IN GROUND
STATE H_2^+ , IN GROUND STATE H_2 , AND IN THE FIRST
EXCITED STATE OF H_2**

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DYNAMICAL GENERATION OF ELECTRON MOTIONS IN GROUND STATE H_2^+ , IN GROUND STATE H_2 , AND IN THE FIRST EXCITED STATE OF H_2 .

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ABSTRACT

Using the recent formulation of Gell-Mann and Hartle for approximating quantum dynamical phenomena by means of classical equations, we simulate electron motions in ground state H_2^+ , in ground state H_2 , and in the first excited state of H_2 . The approach develops approximate initial data first by mathematical bisection. The dynamical calculations are then carried out over short time intervals only, which is consistent with the Gell-Mann and Hartle theory and which is applicable because the phenomena to be studied are periodic. An energy conserving numerical scheme is used so that the energy of a given system will be a numerical invariant. Graphical representations of the electron motions indicate readily electron distributions, or clouds, over various time intervals.

1. Introduction. Quantum dynamics is usually perceived through the time dependent Schrodinger equation, for which related analytical and computational problems appear to be insurmountable at the present time. There is however an alternate approach which can be implemented readily when the dynamical behavior is periodic. This approach is through the quantum dynamical Ehrenfest equations, which are Newtonian dynamical equations for expectation values ^(1,2). Moreover, as shown by Gell-Mann and Hartle, for suitable initial conditions which yield a narrow wave function, Newton's equations themselves provide dynamical approximations over short time periods ⁽³⁾. Of course, for periodic phenomena, knowledge of the character of the first period alone suffices to characterize any phenomenon for all time.

In this paper we will concentrate on electron motions in ground state H_2^+ , in ground state H_2 , and in the first excited state of H_2 . Each case will be preceded by a mathematical bisection technique to generate a reasonable set of initial data, and will be followed then by energy conserving numerical methodology to yield electron motions and electron clouds.

2. The Molecule-Ion H_2^+ . For ground state H_2^+ , the energy E is

$$(2.1) \quad E = - (29.0)10^{-12} \text{ erg,}$$

its average bond length d is

$$(2.2) \quad d = 1.07 \text{ \AA,}$$

and its average vibrational period t^* is

$$(2.3) \quad t^* = (1.45)10^{-14} \text{ sec.}$$

These results are available both experimentally ⁽⁴⁾ and quantum mechanically from the steady state Schrodinger equation ⁽⁵⁾.

Denote the electron in H_2^+ by P_1 and the protons by P_2 and P_3 . Assume the forces are coulombic. In cgs units, for $i = 1, 2, 3$, 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

$$(2.1)$$

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

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

$$(2.2) \quad e_1 = e_2 = -e_3 = (-4.8028)10^{-10} \text{ esu}$$

$$(2.3) \quad m_1 = (9.1085)10^{-28} \text{ g}$$

$$(2.4) \quad m_2 = m_3 = (16724)10^{-28} \text{ g.}$$

For computational convenience, we set $\vec{R}_i = (X_i, Y_i, Z_i)$ and make the transformations

$$(2.5) \quad \vec{R}_i = 10^{12} \vec{r}_i$$

$$(2.6) \quad T = 10^{22} t.$$

System (2.1) transforms then into the following system:

$$(2.7) \quad \frac{d^2 X_1}{dT^2} = (2.5324576) \left(-\frac{X_1 - X_2}{R_{12}^3} - \frac{X_1 - X_3}{R_{13}^3} \right)$$

$$(2.8) \quad \frac{d^2 Y_1}{dT^2} = (2.5324576) \left(-\frac{Y_1 - Y_2}{R_{12}^3} - \frac{Y_1 - Y_3}{R_{13}^3} \right)$$

$$(2.9) \quad \frac{d^2 Z_1}{dT^2} = (2.5324576) \left(-\frac{Z_1 - Z_2}{R_{12}^3} - \frac{Z_1 - Z_3}{R_{13}^3} \right)$$

$$(2.10) \quad \frac{d^2 X_2}{dT^2} = (1.379269)10^{-3} \left(-\frac{X_2-X_1}{R_{12}^3} + \frac{X_2-X_3}{R_{23}^3} \right)$$

$$(2.11) \quad \frac{d^2 Y_2}{dT^2} = (1.379269)10^{-3} \left(-\frac{Y_2-Y_1}{R_{12}^3} + \frac{Y_2-Y_3}{R_{23}^3} \right)$$

$$(2.12) \quad \frac{d^2 Z_2}{dT^2} = (1.379269)10^{-3} \left(-\frac{Z_2-Z_1}{R_{12}^3} + \frac{Z_2-Z_3}{R_{23}^3} \right)$$

$$(2.13) \quad \frac{d^2 X_3}{dT^2} = (1.379269)10^{-3} \left(-\frac{X_3-X_1}{R_{12}^3} + \frac{X_3-X_2}{R_{23}^3} \right)$$

$$(2.14) \quad \frac{d^2 Y_3}{dT^2} = (1.379269)10^{-3} \left(-\frac{Y_3-Y_1}{R_{12}^3} + \frac{Y_3-Y_2}{R_{23}^3} \right)$$

$$(2.15) \quad \frac{d^2 Z_3}{dT^2} = (1.379269)10^{-3} \left(-\frac{Z_3-Z_1}{R_{12}^3} + \frac{Z_3-Z_2}{R_{23}^3} \right)$$

It is system (2.7)-(2.15) which we will solve numerically from selected initial data. However, conservation of the ground state energy is essential numerically, so that we must and will use numerical methodology designed for just such a purpose ⁽⁶⁾.

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

$$(2.16) \quad E = \frac{1}{2}(9.1085)10^{-28}v_1^2 + \frac{1}{2}(16724)10^{-28}(v_2^2 + v_3^2) \\ + (23.06689)10^{-20} \left(-\frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

or, equivalently,

$$(2.17) \quad E = \frac{1}{2}(9.1085)10^{-8}V_1^2 + \frac{1}{2}(16724)10^{-8}(V_2^2 + V_3^2) \\ + (23.06689)10^{-8} \left(-\frac{1}{R_{12}} - \frac{1}{R_{13}} + \frac{1}{R_{23}} \right).$$

3. Numerical Method. The numerical method is divided into two steps. In the first step we determine initial data which are consistent with (1.1)-(1.3). In the second step the actual dynamical behavior is approximated from the initial data so generated.

As shown in Figure 3.1, P_1 is set initially at $(X_1, 0, Z_1)$, P_2 at $(X_2, 0, 0)$, and P_3 at $(-X_2, 0, 0)$, with $X_1 \geq 0$, $Z_1 \geq 0$, $X_2 \geq 0$. The initial velocities are $\vec{V}_1 = (0, V_y, 0)$, $\vec{V}_2 = \vec{V}_3 = 0$, with $V_y > 0$. Begin then by selecting a broad range of values for X_1 , Z_1 , X_2 , as shown in Table 1 and labeled Cases 1-18. For each case, the corresponding value of V_y is determined directly from (1.1) and (2.17) and is recorded in the Table.

Next, for each case, system (2.7)-(2.15) is solved numerically for one half a complete vibration of P_2, P_3 . In the table are recorded in cgs units the values $d_1 = \max\|P_2 P_3\|$, $d_2 = \min\|P_2 P_3\|$, $d = \frac{1}{2}(d_1 + d_2)$ and the time $\frac{1}{2}t'$ for this half vibration. Note from (1.3) that the correct value of $\frac{1}{2}t'$ should be $(0.725)10^{-14}$ sec. The conservative numerical method was run on an Alpha 150 and an Alpha 275, each of which has a 64 bit word. Iteration tolerances were $4(10^{-10})$ for position coordinates and $4(10^{-12})$ for velocity coordinates. The time step was $\Delta T = 1.0$, but was checked occasionally with $\Delta T = 0.2$. A typical FORTRAN program, H2PLUS.FOR, is available for the interested reader (Greenspan⁽⁷⁾).

Figure 3.1
Initial electron and proton configuration

TABLE 1

X_1	Z_1	X_2	V_y	$d_1 (\text{\AA})$	$d_2 (\text{\AA})$	$d (\text{\AA})$	$\frac{t'}{2} (10^{-14} \text{ s})$
0	3000	4000	0.02749697843	0.8	0.4123	0.6061	0.310
0	4000	7000	0.01605936835	1.4	0.1418	0.7709	0.350
0	5000	10000	0.00400324361	2.0	0.0181	1.0091	0.401
0	3000	7000	0.01820890941	1.4	0.1271	0.7636	0.345
0	4000	10000	0.00710756817	2.0	0.0326	1.0163	0.405
0	5000	4000	0.01766724270	0.8	0.4277	0.6139	0.310
2500	3000	4000	0.03078443998	MOLECULE SEPARATES			
2500	4000	7000	0.01827725533	1.4	0.7348	1.0674	0.625
2500	5000	10000	0.00693546911	2.0	1.1067	1.5534	0.605
2500	3000	7000	0.02112716858	1.4	0.7949	1.0975	0.670
2500	4000	10000	0.00957990417	2.0	1.0865	1.5433	0.620
2500	5000	4000	0.01783272795	MOLECULE SEPARATES			
5000	3000	4000	0.02942232997	0.8032	0.7993	0.8013	0.375
5000	4000	7000	0.02311749683	MOLECULE SEPARATES			
5000	5000	10000	0.02110813465	2.0	0.7918	1.3959	0.970
5000	3000	7000	0.02856013547	MOLECULE SEPARATES			
5000	4000	10000	0.01507491669	2.0	0.7624	1.3812	1.025
5000	5000	4000	0.01467574159	MOLECULE SEPARATES			

4. Bisection and the Final Calculation.

The best results are Cases 8 and 10. Both were studied further by bisection, but, because the results were the same, we will discuss only Case 10. To refine the results of Case 10, we then ran Cases 19-22 in Table 2, the final results of which are in the table. Each was run for a complete vibration.

TABLE 2

X_1	Z_1	X_2	V_y	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d(\text{\AA})$	$\frac{1}{2} t'(10^{-14} s)$
2000	3000	7000	0.02009893571	1.4	0.7946	1.10	0.565
3000	3000	7000	0.02235098247	1.4	0.7195	1.06	0.840
4000	3000	7000	0.02528807815	MOLECULE SEPARATES			
5000	3000	7000	0.02856013547	MOLECULE SEPARATES			

Examination next of Cases 10, 19, and 20 leads to the refined cases 23-25 in Table 3, the final results of which are recorded in the table.

TABLE 3

X_1	Z_1	X_2	V_y	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d(\text{\AA})$	$\frac{1}{2} t'(10^{-14} s)$
2600	3000	7000	0.02135687439	1.4	0.7478	1.07	0.695
2700	3000	7000	0.02159427249	1.4	0.7353	1.07	0.725
2800	3000	7000	0.02183920471	1.4	0.7252	1.06	0.795

The results of Case 24 are the best so that we choose as initial data $X_1 = 2700$, $Z_1 = 3000$, $X_2 = 7000$, $V_y = 0.02159427249$. This case is now run for 1 billion time steps, during which P_1 and P_2 complete six full oscillations. In Table 4 are recorded the maxima d_1 and minima d_2 , as well as the time t at which these occur during the oscillations. The average $\bar{d}_1(\text{\AA})$ is 1.40391, the average $\bar{d}_2(\text{\AA}) = 0.73308$, so that the average $\bar{d} = \frac{1}{2}(\bar{d}_1 + \bar{d}_2) = 1.068$. The average time per oscillation is $(8.665)(10^{-14})/6 = 1.444(10^{-14})\text{sec}$. The agreement with both experiment and quantum theory is excellent.

TABLE 4

$d_1 (\text{\AA})$	$d_2 (\text{\AA})$	$t (10^{-14}) s$
1.4		0
	0.7353	0.725
1.3634		1.405
	0.7424	2.065
1.3408		2.700
	0.7230	3.330
1.481		4.170
	0.7228	5.005
1.4165		5.750
	0.7393	6.485
1.4022		7.205
	0.7357	7.915
1.4235		8.665

With regard to trajectories, the electron motion is a complex, spiral like, rotational motion around the X axis. Of course, trajectory complexity is typical in all nondegenerate three-body problems. The motion concentrates for a time around one proton, then drifts to concentrate around the other in an almost periodic fashion. A typical oscillation from P_2 to P_3 is shown projected in the XY plane in Figure 4.1, and under a rotation of axes of 60° in Figure 4.2. Both figures show the concentrated motion around the protons. The time period of the trajectory is $0 \leq t \leq (1.6)10^{-14}$ sec. Also, both figures indicate clearly the electron cloud usually associated with H_2^+ .

Fig. 4.1

Planar projection of the electron
trajectory.

Fig. 4.2

Three dimensional electron trajectory.

5. The Molecule H_2 . For ground state H_2 , the energy E is

$$(5.1) \quad E = - (50.7289)10^{-12} \text{ erg,}$$

the average bond length d is

$$(5.2) \quad d = 0.742 \text{ \AA},$$

and the average vibrational period t^* is

$$(5.3) \quad t^* = (0.759)10^{-14} \text{ sec.}$$

We now extend the methodology of Sections 3 and 4. For this purpose, let P_1, P_3 be electrons and P_2, P_4 protons. At any time t , let $P_i, i = 1, 2, 3, 4$, 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 of the system under coulombic forces are

$$(5.4) \quad m_i \vec{a}_i = \sum_{\substack{j=1 \\ j \neq i}}^4 \frac{e_i e_j}{r_{ij}^2} \frac{\vec{r}_j}{r_{ij}}, \quad i = 1, 2, 3, 4.$$

Transformations (2.5), (2.6) are again introduced for computational convenience. The total energy E of the system is now given by

$$(5.5) \quad E = \frac{1}{2}(9.1085)10^{-28}(v_1^2 + v_3^2) + \frac{1}{2}(16724)10^{-8}(v_2^2 + v_4^2) \\ + 23.06689(10^{-20})\left(-\frac{1}{r_{12}} + \frac{1}{r_{13}} - \frac{1}{r_{14}} - \frac{1}{r_{23}} + \frac{1}{r_{24}} - \frac{1}{r_{34}}\right).$$

or, in the RT variables,

$$(5.6) \quad E = \frac{1}{2}(9.1085)10^{-8}(V_1^2 + V_3^2) + \frac{1}{2}(16724)10^{-8}(V_2^2 + V_4^2) \\ + 23.06689(10^{-8})\left(-\frac{1}{R_{12}} + \frac{1}{R_{13}} - \frac{1}{R_{14}} - \frac{1}{R_{23}} + \frac{1}{R_{24}} - \frac{1}{R_{34}}\right).$$

Initially, we set P_1 at $(X_1, 0, Z_1)$, P_2 at $(X_2, 0, 0)$, P_3 at $(X_1, 0, -Z_1)$ and P_4 at $(-X_2, 0, 0)$. The velocities $\vec{V}_2$ and $\vec{V}_4$ are taken to be zero, while the velocities of P_2 and P_3 are taken to be $(0, VY, 0)$, $(0, -VY, 0)$, respectively. The value VY is chosen positive and is determined from (5.1) and (5.6) once all initial positions are prescribed.

We now choose a variety of initial data and run each case for 150,000,000 time steps. These cases are listed in Table 5. The average maximum value $d_1(\text{\AA})$ and average minimum value $d_2(\text{\AA})$ are recorded in the table. The average time t' for a complete period is also there recorded. We seek to find a set of initial data which will yield $d(\text{\AA}) = \frac{1}{2}(d_1 + d_2) \sim (0.742)\text{\AA}$ and $t' \sim (0.759)10^{-14}\text{sec}$. As before, $\Delta T = 1.0$.

Only three cases in Table 5 seem to yield potentially reasonable results. These are Cases 8, 22, and 26. For Case 8, d is in error by 0.9% while t' is in error by 38%. For Case 22, d is in error by 9.1% while t' is in error by 10.4%. For Case 26, d is in error by

10.6% while t' is in error by 15.3%. We will apply bisection to each case and dispose of Case 26 first.

Bisection for Case 26 yields the results recorded in Table 6. The best result we could obtain is found in Case 29, for which d is in error by 4.4% while t' is in error by 17%. The large increase in accuracy for d is offset by a decrease in accuracy for t' .

TABLE 5 Initial parameter choices

Case	X_1	Z_1	X_2	V_1	d_1 (Å)	d_2 (Å)	d (Å)	$t'(10^{-14} \text{ s})$
1	0	3000	2500	0.03329377412	0.5500	0.4998	0.5249	0.5450
2	0	4000	3500	0.02589577453	0.7000	0.3962	0.5481	0.4460
3	0	5000	4500	0.02035480818	0.9000	0.2849	0.5925	0.4625
4	0	3000	4500	0.02475086432	0.9000	0.3387	0.6194	0.5760
5	750	3000	2500	0.03343587395	0.5790	0.4999	0.5395	0.4525
6	750	4000	3500	0.02599955202	0.7083	0.4033	0.5558	0.4575
7	750	5000	4500	0.02043097925	0.9087	0.3393	0.6240	0.5100
8	750	3000	4500	0.02513779382	0.8495	0.6478	0.7486	0.4688
9	750	5000	2500	0.02210800344	0.6076	0.5000	0.5538	0.4575
10	1500	3000	2500	0.03360270073	0.7740	0.4974	0.6357	0.5640
11	1500	4000	3500	0.02623506999	0.6953	0.4306	0.5630	0.4710
12	1500	5000	4500	0.02062889280	0.9006	0.3153	0.6079	0.5300
13	1500	3000	4500	0.02623821490	0.8541	0.3809	0.6174	0.5240
14	1500	4000	2500	0.02727255122	0.6727	0.5002	0.5865	0.4925
15	1500	5000	3500	0.02201936253	0.6950	0.4415	0.5683	0.4675
16	3000	3000	2500	0.03143682515	0.8641	0.5000	0.6841	0.5600
17	3000	4000	3500	0.02616869595	0.7017	0.5584	0.6301	0.5500
18	3000	5000	4500	0.02099031113	0.9014	0.3101	0.6057	0.5100
19	3000	3000	4500	0.02960887873	1.1041	0.2713	0.6885	0.6150
20	3000	4000	2500	0.02492431491	0.7963	0.4975	0.6469	0.5270
21	3000	5000	3500	0.02129827379	0.7113	0.5090	0.6102	0.5250
22	4500	3000	2500	0.02417234606	1.2015	0.4180	0.8098	0.6800
23	4500	4000	3500	0.02365205438	0.7015	0.6952	0.6984	0.5780
24	4500	5000	4500	0.02033127101	0.8465	0.4023	0.6244	0.5090
25	4500	3000	4500	0.03101278747	0.8466	0.4020	0.6243	0.5110
26	4500	4000	2500	0.01951372817	0.9542	0.6873	0.8208	0.6431
27	4500	5000	3500	0.01892684707	0.7150	0.5944	0.6547	0.4763

TABLE 6 Parameter refinements

X_1	Z_1	X_2	VY	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d(\text{\AA})$	$t'(10^{-14} \text{ sec})$
4600	4000	2700	0.02024231712	0.9544	0.4304	0.6929	0.5500
4800	4000	2700	0.01935244938	1.1495	0.3999	0.7747	0.6300
4700	4000	2700	0.01980382359	0.9904	0.4135	0.7020	0.6150
4700	4100	2700	0.01934515946	0.7676	0.5018	0.6347	0.4360
4600	4100	2700	0.01977454142	0.9194	0.4589	0.6892	0.5000
4800	4100	2700	0.01890291760	0.9791	0.4650	0.7220	0.5890
4700	3900	2700	0.02026122471	0.8855	0.4566	0.6711	0.5160
4600	3900	2700	0.02070970571	0.9385	0.4267	0.6826	0.5800
4800	3900	2700	0.01979830040	0.9971	0.5387	0.7679	0.5700

Bisection for Case 22 yields the results in Table 7. The result of Case 40 is already superior to Case 8, so that Case 8 is now discarded. Cases 37, 39, and 40 show quite clearly a dilemma which one faces. For Case 39, t' is in error by 0.03% while d is in error by 16.7%. For Case 40, d is in error by 0.01% while t' is in error by 24%. For Case 37, d is in error by 1.3% but t' is in error by 8.6%. We are simply unable to approximate both d and t' to within 5% error. One of d and t' can always be approximated quite accurately, but never both.

TABLE 7 Additional parameter refinements

X_1	Z_1	X_2	V_1	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d(\text{\AA})$	$t'(10^{-14} \text{ s})$
4500	3200	2700	0.02450993946	0.9948	0.5092	0.7520	0.6938
4500	3000	2700	0.02547679891	1.1115	0.4615	0.7865	0.6375
4500	3000	2300	0.02265776565	1.2347	0.4980	0.8663	0.7588
4500	3200	2500	0.02326220061	0.9715	0.5139	0.7427	0.5750
4500	2800	2500	0.02506217016	1.2987	0.3960	0.8473	0.7750
4700	2900	2500	0.02332158312	1.0934	0.4938	0.7936	0.6500
4300	3200	2500	0.02437897766	0.9511	0.4388	0.6950	0.6038
4300	3100	2700	0.02605912690	1.2773	0.3449	0.8111	0.7250
4700	3200	2300	0.02052111578	1.2409	0.3632	0.8021	0.5700

To confront this failure, we considered next the possibility that P_1 's initial velocity was not in the Y direction only. For this purpose, we set $\vec{V}_1 = (VX, VY, 0)$. The values of VX and VY are determined by selecting, at random, an angle of 30° , 34° , or 60° for $\vec{V}_1$ relative to the Y axis. For symmetry, we set $\vec{V}_3 = (VX, -VY, 0)$. The resulting 24 cases considered are recorded in Table 8. Again, the results are poor.

TABLE 8 Additional parameter choices

X_1	Z_1	X_2	VX	VY	d (Å)	t (10^{-14} sec)
0	3000	2500	0.023542253	0.023542253	0.8248	0.7850
0	4000	3500	0.012947887	0.022426398	0.7090	0.4381
0	5000	4500	0.014393023	0.014393023	0.7224	0.6367
0	3000	4500	0.012375432	0.021434877	0.7226	0.6330
0	4000	2500	-0.023992662	0.013852170	1.0073	1.1525
0	5000	3500	0.011042759	0.019126619	0.7096	0.6370
1500	3000	2500	0.016801350	0.029100792	0.6934	0.5638
1500	4000	3500	0.018550995	0.018550995	0.7761	0.6175
1500	5000	4500	-0.017865145	0.010314446	0.8745	0.8540
1500	3000	4500	-0.022722960	0.013119107	0.9574	0.7563
1500	4000	2500	0.019284606	0.019284606	0.7644	0.6270
1500	5000	3500	0.011009680	0.019069327	0.7075	0.5600
3000	3000	2500	-0.027225089	0.015718413	0.9375	0.8513
3000	4000	3500	0.018504062	0.018504062	0.7178	0.6023
3000	5000	4500	0.014842391	0.014842391	0.7588	0.6145
3000	3000	4500	-0.025642041	0.014804439	0.7704	0.6200
3000	4000	2500	0.012462157	0.021585089	0.7467	0.6425
3000	5000	3500	-0.0184444845	0.010649137	0.7880	0.5225
4500	3000	2500	-0.020933866	0.012086173	1.0050	0.9238
4500	4000	3500	0.011826027	0.020483280	0.8072	0.7950
4500	5000	4500	-0.017607397	0.010165636	0.9253	0.6752
4500	3000	4500	0.021929352	0.021929352	0.6965	0.7070
4500	4000	2500	-0.016899384	0.009756864	0.8419	0.8985
4500	5000	3500	0.009463424	0.016391130	0.6558	0.5310

6. The H₂ Molecule, Revisited. In this section we consider another possible approach to simulating a dynamical H₂ molecule using Newtonian mechanics. this approach is motivated by the interest in recent years in electron attraction, real or apparent ⁽⁸⁻¹³⁾. Nobelists Bardeen, Cooper, and Schrier required electron attraction in their quantum mechanical theory of superconductivity. Panarella showed that electron attraction is viable in his quantum mechanical study of photons. Ashoori has shown that an "apparent" electron attraction results from large magnetic forces in "artificial" atoms. Greenspan has shown that correct bond lengths and periods result for all diatomic molecules through O₂ by assuming electron attraction as does the correct bond angle for the water molecule. Nobelist Dehmelt has hypothesized sub quark elements for electron structure, which might have relevant implications. No direct experimental evidence is available to establish whether or not electron attraction is a real or an apparent phenomenon, although it has proved to be of theoretical value. We continue then in this spirit and will produce results which are excellent. The changes required in the discussion of Section 5 are that $e_1 e_3$ in (5.4) be replaced by $-e_1 e_3$, r_{13} in (5.5) be replaced by $-r_{13}$, an R_{13} in (5.6) be replaced by $-R_{13}$.

It should be noted now that the discussion which follows is analogous to, but more extensive and uses a smaller time step, than the discussion in Greenspan ⁽¹⁴⁾.

Consider then the 30 cases recorded in Table 9. Each was run for 100000000 time steps. The average maximum $d_1(\text{\AA})$, average minimum $d_2(\text{\AA})$, average $d(\text{\AA}) = \frac{1}{2}(d_1 + d_2)$, and average period t' are recorded in the Table. the results in Table 9 indicate that Cases 2, 8, and 14 are already almost correct. Application of bisection led to the Cases reported in Table 10, each of which was run for 250000000 time steps. Several cases are very good. Case 40, for example, yields an error of 3.9% for d and 0.7% for t' , while Case 34 yields an error of 2.1% for d and 3.4% for t' .

For Case 40 the electron cloud generated by P_3 is toroidal, and the electron moves back and forth between P_1 and P_2 several times. The three dimensional motion is shown in Figure 6.1. Its projection in the XZ plane is shown in Figure 6.2. In both figures, the motion is for the real time $t = (0.754)10^{-14}$ sec. the motion for Case 34 is entirely analogous.

TABLE 9 Initial data choices

	X_1	Z_1	X_2	VY	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d(\text{\AA})$	$r'(10^{-14} \text{ sec})$
	0	3000	2500	0.04418854972	1.0909	0.4999	0.7954	0.7225
	0	4000	3500	0.03610686274	0.8471	0.6998	0.7734	0.7100
	0	5000	4500	0.03034484692	0.9000	0.6810	0.7905	0.7350
	0	3000	4500	0.03816749685	0.9000	0.5714	0.7357	0.6900
	0	4000	2500	0.03742519009	1.1763	0.5000	0.8382	0.7500
	0	5000	3500	0.03153191415	0.9024	0.7000	0.8012	0.7325
	1000	3000	2500	0.04435588462	1.2426	0.5000	0.8713	0.9300
	1000	4000	3500	0.03623304387	0.8818	0.7000	0.7909	0.7425
	1000	5000	4500	0.03043345495	0.9000	0.6944	0.7973	0.7375
	1000	3000	4500	0.03861261923	0.9000	0.7539	0.8270	0.8925
	1000	4000	2500	0.03730504470	1.3553	0.5000	0.9277	0.9275
	1000	5000	3500	0.03151988519	0.9296	0.6990	0.8142	0.7550
	1500	3000	2500	0.04442177426	1.3917	0.5000	0.9459	1.0150
	1500	4000	3500	0.03635097380	0.9218	0.6999	0.8094	0.7725
	1500	5000	4500	0.03052937499	0.9000	0.7030	0.8015	0.7575
	1500	3000	4500	0.03914839017	0.9245	0.7384	0.8315	0.7625
	1500	4000	2500	0.03710669008	1.5244	0.5000	1.0122	0.9400
	1500	5000	3500	0.03148561331	0.9634	0.7000	0.8317	0.7800
	3000	3000	2500	0.04280685117	1.9720	0.5000	1.2360	1.3200
	3000	4000	3500	0.03630309968	1.1151	0.7200	0.9175	0.8600
	3000	5000	4500	0.03077474095	0.9000	0.8347	0.8673	0.8300
	3000	3000	4000	0.04148298725	0.9244	0.7534	0.8389	0.8100
	3000	4000	2500	0.03541660447	1.9472	0.5000	1.2236	1.3000
	3000	5000	3500	0.03098560933	1.1262	0.7000	0.9131	0.8500
	4500	3000	2500	0.03779490502	MOLECULE SEPARATES			
	4500	4000	3500	0.03453308667	1.6216	0.7000	0.9131	1.0200
	4500	5000	4500	0.03032906362	1.0647	0.9000	0.9823	0.9600
	4500	3000	4500	0.04249641771	1.0588	0.8000	0.9294	0.7600
	4500	4000	2500	0.03184179621	MOLECULE SEPARATES			
	4500	5000	3500	0.02940607181	1.4181	0.7000	1.0590	0.9100

Finally, Case 40 was run for five full oscillations. These results are recorded in Table 11. Over the entire five oscillations, the average d is $0.7742 \text{ \AA}$ and the average t' is $0.748(10^{-14})$ sec, which are in error 4.3% and 1.4%, respectively.

TABLE 10 Refined parameter choices

	X_1	Z_1	X_2	VY	$d_1(\text{\AA})$	$d_2(\text{\AA})$	$d(\text{\AA})$	$t'(10^{-14} \text{ sec})$
	1000	2600	3800	0.03763349834	0.7714	0.7596	0.7660	0.7300
	1000	3600	3650	0.03797633715	0.8203	0.7310	0.7275	0.7520
	1000	3600	3950	0.03728215948	0.7902	0.7348	0.7625	0.7312
	1000	3450	3800	0.03838758421	0.7619	0.7595	0.7607	0.7330
	1000	3750	3800	0.03689529324	0.7883	0.7613	0.7747	0.7240
	850	3600	3800	0.03756426185	0.7651	0.7595	0.7623	0.7313
	1150	3600	3800	0.03771111074	0.7802	0.7596	0.7699	0.7340
	1000	3500	3700	0.03837620224	0.7909	0.7396	0.7652	0.7190
	1000	3600	3700	0.03786315384	0.7974	0.7397	0.7586	0.7105
	1000	3700	3700	0.03735752925	0.8089	0.7395	0.7742	0.7538

TABLE 11 Five oscillations of Case 40

$d_1(\text{\AA})$	$d_2(\text{\AA})$	$t(10^{-14} \text{ s})$
	.7400	0
.8096		.370
	.7394	.750
.8080		1.115
	.7389	1.495
.8078		1.860
	.7394	2.240
.8092		2.605
	.7397	2.980
.8099		3.360
	.7395	3.740

Fig6.1 Electron cloud for Case 40.

Fig6.2 Projection of the electron cloud for Case 40

7. The $\sum_u^{1+}$ State of H_2 . The first excited state of H_2 , that is, the $\sum_u^{1+}$ state is unique in that most excited states have bond lengths and vibrational frequencies very close to those of ground state $H_2^{+(4,5)}$. However the $\sum_u^{1+}$ state has bond length d given by

$$(7.1) \quad d = 1.2927 \text{ \AA}$$

and vibrational period t^* given by

$$(7.2) \quad t^* = (2.4568)10^{-14} \text{ sec,}$$

which differ distinctly from (2.2) and (2.3). Its energy E is ⁽⁴⁾

$$(7.3) \quad E = (-32.51536)10^{-12} \text{ erg.}$$

In addition, it is claimed that one atom of the molecule is normal while the other is excited ⁽⁵⁾.

The lack of electron symmetry in the $\sum_u^{1+}$ state will require exceptionally accurate numerical simulation. However, before describing the simulation which was successful, let us indicate that we assume electron attraction, since considerations entirely analogous to those to be discussed, never yielded correct results for electron repulsion.

We begin as in Section 5 and assume that e_1e_3 is replaced by $-e_1e_3$ in (5.4), r_{13} is replaced by $-r_{13}$ in (5.5), R_{13} is replaced by $-R_{13}$ in (5.6), and that the value of E in (7.3) is used in both (5.5) and (5.6). conservative numerical methodology is implemented with a variable time step according to the following rule. At any time step, let $\bar{R} = \min |R_{ij}|$, $i = 1, 2, 3, 4$; $j = 1, 2, 3, 4$; $i \neq j$.

Then if	$\bar{R} \geq 2000,$	$\Delta T = 1.0$	;
	$2000 > \bar{R} \geq 1000,$	$\Delta T = 0.2$	;
	$1000 > \bar{R} \geq 750,$	$\Delta T = 0.02$	;
	$750 > \bar{R} \geq 500,$	$\Delta T = 0.002$	;
	$500 > \bar{R} \geq 200,$	$\Delta T = 0.0002$	;
	$200 > \bar{R}$	$\Delta T = 0.00002$	.

Over 100 sets of initial data were studied with extensive bisection implementation. From these, the following set of initial data emerged:

$X(1) = -1409.90053737$	,	$VX(1) = 0.06116248586$
$Y(1) = -2800.96212959$	,	$VY(1) = 0.01203025741$
$Z(1) = 37083.75875130$	,	$VZ(1) = 0.00533622272$
$X(2) = 4547.94783095$	,	$VX(2) = -.00000565964$

Y(2) = 492.05314401	,	VY(2) = 0.00000551882
Z(2) = 552.41757524	,	VZ(2) = 0.00000976669
X(3) = -1004.900577079098	,	VX(3) = 0.00548586693
Y(3) = -672.99845721	,	VY(3) = -0.01892571304
Z(3) = -4877.59128996	,	VZ(3) = 0.00476896279
X(4) = -4546.63271294	,	VX(4) = -0.00000068448
Y(4) = 1318.76654753	,	VY(4) = 0.00001707969
Z(4) = -547.46474262	,	VZ(4) = -0.00001527034

With these data as initial data, one has $|P_2 P_4| = 0.9198 \text{ \AA}$. Computer simulation yielded monotonic increasing values of $|P_2 P_4|$ to a maximum of $1.5836 \text{ \AA}$ at $t = (1.24)10^{-14}$ sec. From this half period one can extrapolate to yield

$$(7.4) \quad d = \frac{1}{2}(0.9198 + 1.5836) = 1.2517 \text{ \AA}$$

$$(7.5) \quad t' = 2(1.24)10^{-14} = (2.48)10^{-14} \text{ sec},$$

which are in error 3.2% and 0.9% respectively. the variation of d with t is shown in the left half of Figure 7.1. Continuation of this calculation then reveals that $|P_2 P_4|$ reaches a minimum value of $1.133 \text{ \AA}$ in an oscillatory fashion at $t = (2.47)10^{-14}$ sec. This dependence is shown in the right half of Figure 7.1. If one now calculates d and t' over the entire period, one finds

$$(7.6) \quad d = [\frac{1}{2}(0.9198 + 1.133) + 1.5836]/2 = 1.305 \text{ \AA}$$

$$(7.7) \quad t' = (2.47)10^{-14} \text{ sec}.$$

These results are in error 1.0% and 0.5%, respectively. No successive calculation ever repeated this degree of accuracy.

Figure 7.2 shows the very large orbital type motion of P_1 in three dimensions, while Figure 7.3 shows the projection of this motion in the XZ plane. The distance P_1 maintains to the line joining P_2 and P_4 is always approximately $3.7 \text{ \AA}$. The figures show four revolutions of P_1 , which occur in the time $(0.635)10^{-14}$ sec. Over this same period, Figures 7.4 and 7.5 show the three dimensional motion and projected two dimensional motion of P_3 . This motion is of a complex toroidal nature, is distinctly affected by the nonsymmetric interaction with P_1 , and has an average radius comparable to that of a ground state H atom.

8. Summary. We have shown how to implement the Gell-Mann and Hartle classical theory for approximating quantum dynamical motion by applying bisection and conservative numerical methodology to each of H_2^+ , H_2 , and the first excited state of H_2 . For the latter two cases, electron attraction proved to be essential in order to obtain bond lengths and vibrational periods which were both in error by less than 5%.

It is important to observe that no result depends on any quantum mechanical result. The total energy, bond length, and vibrational frequency, which are assumed in our approach, are available directly from experiment. Moreover, the dynamical, toroidal electron trajectories which have been displayed are not available quantum mechanically, since no methodology is at present available for solving the related time dependent Schrodinger equation.

Figure 7.1 Diameter variation with time for the first excited state of H_2 .

Figure 7.2 Four complete rotations of P_1

Figure 7.3. Two dimensional projection
of the motion shown in Figure 7.2

Fig. 7.4 Three dimensional motion of
of P_3 in the same time as the three
dimensional motion of P_1 shown in Fig. 7.2.

Fig. 7.5 Projection in the YZ plane of the three dimensional motion of P_3 shown in Fig. 7.4

REFERENCES

1. D. Park, INTRODUCTION TO QUANTUM THEORY, McGraw-Hill, N.Y., 1964.
2. P.R. Holland, THE QUANTUM THEORY OF MOTION, Cambridge Univ. Press, Cambridge, 1993.
3. M. Gell-Mann and J.B. Hartle, "Classical Equations for Quantum Systems", UCSBTH-91-15, Univ. Cal. Santa Barbara, n.d.
4. G. Herzberg, MOLECULAR SPECTRA AND MOLECULAR STRUCTURE, Krieger, Malabar, FL, 1989.
5. L. Pauling and E.B. Wilson, INTRODUCTION TO QUANTUM MECHANICS, Dover, N.Y., 1963.
6. D. Greenspan, "Deterministic Computer Physics", Int. J. Theor. Phys., 21, 1982, p. 505.
7. D. Greenspan, "A New Method for Approximating Quantum Dynamical Phenomena Over Short (and Sometimes Long) Time Periods", TR 304, Math. Dept., Univ. Texas at Arlington, 1995.
8. J. Bardeen, L. N. Cooper, and J.R. Schrieffer, "Theory of Superconductivity", Phys. Rev., 108, 1957, p. 1175.
9. E. Panarella, "Nonlinear Behaviour of Light at Very Low Densities: The 'Photon Clump' Model", in QUANTUM UNCERTAINTIES, Plenum, N.Y., 1987.
10. R. C. Ashoori, "Electrons in Artificial Atoms", Nature, 379, 1996, p. 413.
11. D. Greenspan, "On Electron Attraction in the Diatomic Bond", Physics Essays, 5, 1992, p. 554.
12. D. Greenspan, "A Semiclassical, Dynamical Model of the Water Molecule", to appear in Physica Scripta.
13. H. Dehmelt, "Experiments on the Structure of an Individual Elementary Particle", Science, 247, 1990, p. 539.
14. D. Greenspan, "Electron Attraction as a Mechanism for the Chemical Bond of Ground State H_2 ", Physica Scripta, 52, 1995, p. 267.