Numerical Approximation of Energy Perturbation in the Hydrogen Molecule

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Abstract

We can see that by means of computer aid it is fairly easy to find the numerical approximation of energy perturbation in the hydrogen molecule, and to plot this energy as a function of the distance between the nuclei of said molecule.

Resumen

Se ha usado el computador electrónico para encontrar la energía de perturbación en la molécula de hidrógeno, y para representar gráficamente esta energía en función de la distancia entre los núcleos de dicha molécula.

When the two atoms of the hydrogen molecule, H_2, are separated by a distance R = 0.5 Å (which is large compared with the size of the first Bohr orbit), it is easy to associate each electron with its own parent nucleus, but, when $R < 0.5$ Å, there is no way to identify each electron as corresponding to a given nucleus. In this last case, the two hydrogen atoms are brought together to form the hydrogen molecule.[1] The binding in the hydrogen molecule is a simple example of a covalent bond.

FAINDING AN ANALYTICAL EXPRESSION OF ENERGY PERTURBATION.[2]

Consider the protons as infinitely massive, and neglect spin-dependent terms. The system comprises two hydrogen nuclei, A and B, and two electrons, whose coordinates we designate by 1 and 2 (Fig. 1).

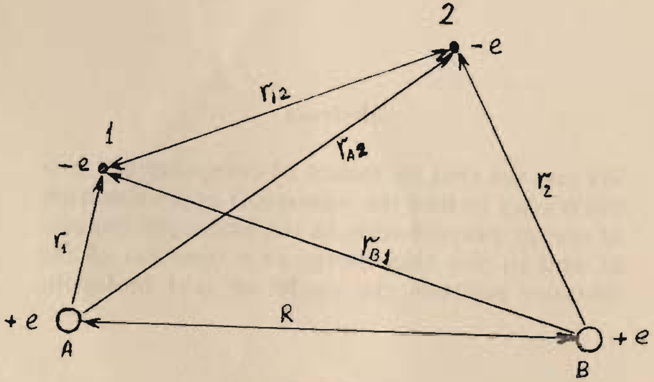

FIGURE 1

Coordinates used for the hydrogen molecule.

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[1] Weidner and Sells, *Elementary Modern Physics*, pp. 521-522.

[2] Pauling and Wilson, *Introduction to Quantum Mechanics*, pp. 340-343. Born, *Atomic Physics*, pp. 466-469. Schiff, *Quantum Mechanics*, pp. 449-451. Saxon, *Elementary Quantum Mechanics*, pp. 391-392.

Using the coordinate system shown in Fig. 1, the Hamiltonian can be written as

$$H = \left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{e^2}{r_1} + \frac{e^2}{r_2} - \frac{e^2}{R} + \frac{e^2}{r_{A2}} + \frac{e^2}{r_{B1}} - \frac{e^2}{r_{12}} \right)$$

Then, the wave equation for the two electrons corresponding to fixed positions of the two nuclei is

$$\nabla_1 \psi(\vec{r}_1, \vec{r}_2) + \nabla_2 \psi(\vec{r}_1, \vec{r}_2) + \frac{4\pi^2 m}{h^2} H \psi(\vec{r}_1, \vec{r}_2) = 0.$$

For «small» R, as it was used in the computer program, the wave functions are

$$\psi_+ (\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2 + 2\Delta^2}} \left\{ \phi_0(r_1)\, \phi_0(r_2) + \phi_0(r_{A2})\, \phi_0(r_{B1}) \right\}$$

$$\psi_- (\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2 - 2\Delta^2}} \left\{ \phi_0(r_1)\, \phi_0(r_2) - \phi_0(r_{A2})\, \phi_0(r_{B1}) \right\}.$$

ψ_+ is symmetric in the positional coordinates of the two electrons and also in the positional coordinates of the two nuclei, whereas ψ_- is antisymmetric in both of these sets of coordinates. $\varnothing_0$ (r_1)

and $\varnothing_0$ (r_2) are ground-state hydrogen wave functions. $\triangle$ is the orthogonality integral.

$$\Delta^2 = \int \phi_0(r_1)\, \phi_0(r_2)\, \phi_0(r_{A2})\, \phi_0(r_{B1})\, d^3r_1\, d^3r_2 \quad , \qquad [3]$$

or

$$\Delta^2 = e^{-2D} \left(1 + D + \frac{1}{3} D^2\right)^2 , \qquad [4]$$

where $D = \dfrac{R}{a_0}$.

The interaction energy of the molecule which arises when the atoms approach one another is

$$V' = \frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{B1}} - \frac{e^2}{r_{A2}} .$$

The formulas for the energy are given in Pauling and Wilson's book, p. 343, as

$$E_s = 2E + \frac{e^2}{R} + \frac{2J + J' + 2K\Delta + K'}{1 + \Delta^2} \tag{a}$$

$$E_A = 2E + \frac{e^2}{R} + \frac{2J + J' - 2K\Delta - K'}{1 - \Delta^2} ,$$

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[3] Saxon, *op. cit.* p. 392.

[4] Pauling and Wilson, *op. cit.* p. 328 and p. 341.

where

E is a constant.
J represents the Coulomb interaction of an electron in a 1s orbital on nucleus A with nucleus B.
J' represents the Coulomb interaction of an electron in a 1s orbital on nucleus A with an electron in a 1s orbital on nucleus B.
K is called a resonance or exchange integral, since $\varnothing_0$ (r_1) and $\varnothing_0$ (r_2) occur initially.
K' is the resonance or change integral corresponding to J'.

That is,

$$J = \int \phi_0(r_{B1}) \left(-\frac{e^2}{r_{B1}}\right) \phi_0(r_1)\, d^3r_1 = \frac{e^2}{a_0} \left\{-\frac{1}{D} + e^{-2D}\left(1 + \frac{1}{D}\right)\right\} .$$

$$J' = e^2 \iint \frac{\{\phi_0(r_1)\, \phi_0(r_2)\}^2}{r_{12}}\, d^3r_1\, d^3r_2 = \frac{e^2}{a_0} \left\{ \frac{1}{D} - e^{-2D} \left(\frac{1}{D} + \frac{11}{8} + \frac{3}{8}D + \frac{1}{6}D^3\right)\right.$$

$$K = \int \phi_0(r_{B1}) \left(-\frac{e^2}{r_{B1}}\right) \phi_0(r_1)\, d^3r_1 = -\frac{e^2}{a_0}\, e^{-D} (1 + D)$$

$$K' = e^2 \iint \frac{\phi_0(r_1)\, \phi_0(r_2)\, \phi_0(r_{A2})\, \phi_0(r_{B1})}{r_{12}}\, d^3r_1\, d^3r_2$$

$$= -\frac{e^2}{5a_0} \left[-e^{-2D} \left(-\frac{25}{8} + \frac{23}{4}D + 3D^2 + \frac{1}{3}D^3\right) + \frac{6}{D}\left\{\Delta^2(\gamma + \log D) + \Delta'^2 Ei(-4D) - 2\Delta\Delta' Ei(-2D)\right\}\right] .$$

where

$\gamma = \ln C = 0.577215665$ (Euler's constant)

$\Delta' = e^{D}\left(1 - D + \frac{1}{3}D^2\right)$.

Ei is the integral logaritm and from JAHNKE-EMDE-LÖSCH,[5] for y > 2,

$$\mathrm{Ei}(-y) = \frac{e^{-y}}{-y}\left(0.9999965 - \frac{0.9989710}{y} + \frac{1.9487646}{y^2} - \frac{4.9482092}{y^3} + \frac{11.7850792}{y^4} - \frac{20.4523840}{y^5} + \frac{21.1491469}{y^6} - \frac{9.5240410}{y^7} \pm 0.35 \times 10^{-5} \right).$$

EVALUATION OF ENERGY PERTURBATION.

From equations (a) we have

$$E_+ = \frac{e^2}{R} + \frac{2J + J' + 2K\Delta + K'}{1 + \Delta^2}$$

$$E_- = \frac{e^2}{R} + \frac{2J + J' - 2K\Delta - K'}{1 - \Delta^2}, \qquad \text{(b)}$$

where E + corresponds to a bound state, and E − corresponds to an unbound state, as we will see by plotting the results of their numerical approximations (see Fig. 2 and Appendix B).

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[5] Jahnke-Emde-Lösch, *Tables of Higher Functions*, p. 18.

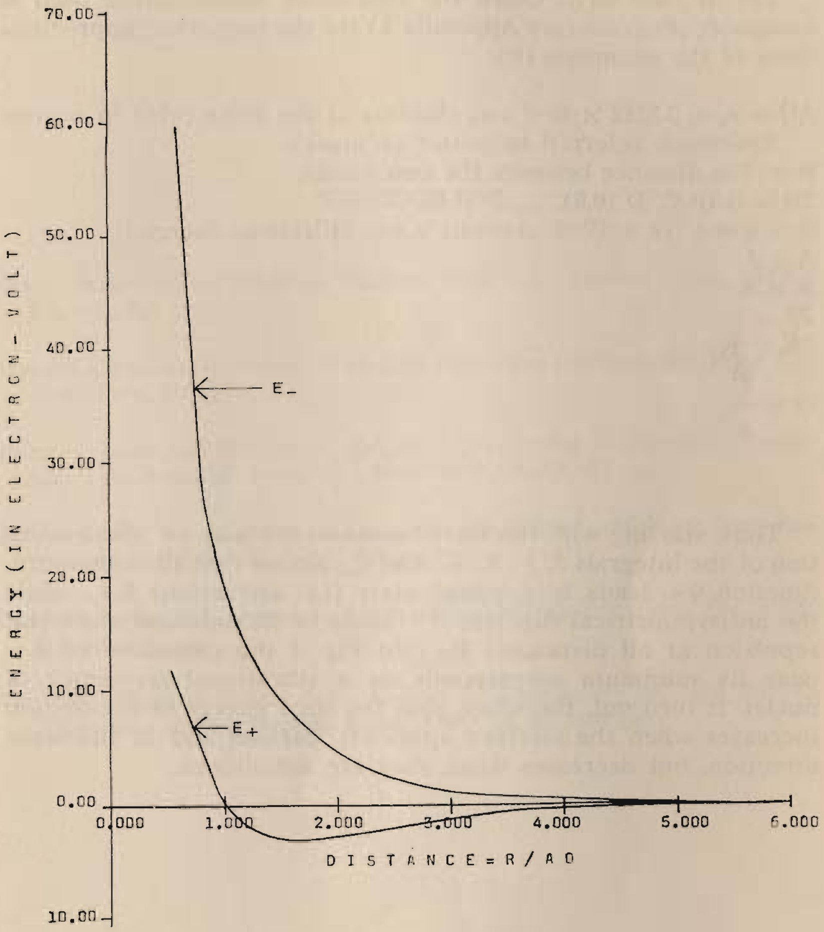

FIGURE 2

The energies of the bound and unbound states as functions of the distance between the nuclei. (Plotting, by a computer plotter, from computer program and results given in Appendices A and B.)

Let us now write down the equivalent nomenclature used in computer program (see Appendix A) for the numerical approximations of the equations (b).

$AO = a_0 = 0.5282 \times 10^{-8}$ cm. (Radius of the Bohr orbit in normal hydrogen, referred to center of mass.)
R = The distance between the two nuclei.
DI = D (0.6), D (0.8), ..., D (6.0).
$E = e = 4.770 \times 10^{-10}$ absolute e.s.u. (Electron charge.)
A = J.
B = K.
PJ = J'.
PK = K'.
$Q = \frac{e^2}{R}$.

Thus, starting with the wave functions $\psi +$ and $\psi -$, the evaluation of the integrals J, J', K, K', and $\triangle$, shows that the symmetric function $\psi +$ leads to a bound state (i.e. attraction) $E +$, while the antisymmetrical function $\psi -$ leads to an unbound state (i.e. repulsion at all distances) $E -$. In Fig. 2 the curvature of $E +$ near its minimum corresponds to a vibrational frequency of nuclei. It turn out, therefore, that the total energy of the system increases when the electron spins are parallel and in the same direction, but decreases when they are antialigned.

ACKNOWLEDGMENT.

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APPENDIX A

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      PROGRAM DNE (INPUT,OUTPUT,PLOT,TAPE5=INPUT,TAPE6=OUTPUT)
C  NUMERICAL APPROXIMATION OF THE ENERGY PERTURBATION
C  IN THE HYDROGEN MOLECULE
      COMMON X,A0,DELTA,E
      DIMENSION DISTAN(30),EPLUS(30),EMINUS(30)
      CALL PLOTS
      EMIN=0.0
      EMAX=60.
      DMAX=6.0
      DMIN=0.0
      AE=EMAX/6.
      CALL PLOT(0.0,3.0,-3)
      CALL AXIS(0.0,0.0,15HDISTANCE = R/A0,-15,6.0,0.,0.0,1.0,0)
      CALL AXIS(0.0,-3.,24HENERGY(IN ELECTRON-VOLT),+24,10.0,90.,
     1 -EMAX/2.0,AE,-1)
      WRITE(6,6)
    6 FORMAT(12X, ≠ENERGY PERTURBATION IN THE HYDROGEN MOLECULE,
     1 (E+,E-,J,K,J(PRIME),K(PRIME),AND E**2/R  IN ELECTRON-VOLT)≠,///
     2 10X,≠E+≠,6X,≠E-≠,4X,≠DISTAN=R/A0≠,4X,≠R (CM.)≠,8X,≠J≠,
     2 13X,≠K≠,8X,≠DELTA≠,3X,≠DELTA**2≠,3X,≠J(PRIME)≠,
     2 5X,≠K(PRIME)≠,7X,≠E**2/R≠/)
      A0=.5282E-08
C  THE ENERGY E+ (OR E-) IN ELECTRON-VOLT
      DO 8 I=1,28
      DI=I+2
      DISTAN(I)=2.0*DI/10.
C  R IN CENTIMETER
      R=DISTAN(I)*A0
      X=DISTAN(I)
      E=4.770/(10.**10)
C  ELECTRONIC CHARGE IN ABSOLUTE E.S.U.
      A=(E**2/A0)*(-1./X+EXP(-2*X)*(1.+1./X))
      B=(-E**2/A0)*EXP(-X)*(1.+X)
      DELTA=EXP(-X)*(1.+X+X**2/3.)
      PJ=(E**2/A0)*(1./X-EXP(-2*X)*(1./X+11./8.+3*X/4.+X**2/6.))
      CALL INTLOG(PK)
      EPLUS(I)=(E**2/R)+(2*A+PJ+2*DELTA*B+PK)/(1.0+DELTA**2)
      EMINUS(I)=(E**2/R)+(2*A+PJ-2*DELTA*B-PK)/(1.0-DELTA**2)
      Q=E**2/R
      TANT=+6285E+12
      EPLUS(I)=EPLUS(I)*TANT
      EMINUS(I)=EMINUS(I)*TANT
      A=A*TANT
      B=B*TANT
      PJ=PJ*TANT
      PK=PK*TANT
      Q=Q*TANT
      TEMP=DELTA**2
      WRITE(6,7)EPLUS(I),EMINUS(I),DISTAN(I),R,A,B,DELTA,TEMP,PJ,PK,Q
    7 FORMAT(6X,3F8.3,E14.3,2F14.5,2F8.3,2F14.5,E14.3)
    8 CONTINUE
      DISTAN(29)=0.0
      DISTAN(30)=1.0
      EPLUS(29)=0.0
      EPLUS(30)=AE
      CALL LINE(DISTAN,EPLUS,28,1,0,0)
      DISTAN(29)=0.0
      DISTAN(30)=1.0
      EMINUS(29)=0.0
      EMINUS(30)=AE
      CALL LINE(DISTAN,EMINUS,28,1,0,0)
      CALL PLOT(0,0,999)
      STOP
      END
```

```
      SUBROUTINE INTLOG(PK)
      COMMON X,A0,DELTA,E
      GAMMA=.577215665
      PDELTA=EXP(X)*(1.-X+X**2/3.)
C FOR THE CASE X GREATER THAN 2 WE HAVE THE FOLLOWING EXPRESSION
      FI1=(EXP(-4*X)/(-4*X))*(.9999965-.9989710/(4*X)+
     1 1.9487646/((4*X)**2)-4.9482092/((4*X)**3)+
     1 11.7850792/((4*X)**4)-20.4523840/((4*X)**5)
     1 +21.1491469/((4*X)**6)-9.5240410/((4*X)**7))
      FI2=(EXP(-2*X)/(-2*X))*(.9999965-.9989710/(2*X)+
     1 1.9487646/((2*X)**2)-4.9482092/((2*X)**3)+
     1 11.7850792/((2*X)**4)-20.4523840/((2*X)**5)
     1 +21.1491469/((2*X)**6)-9.5240410/((2*X)**7))
      PK=(E**2/(5*A0))*(-EXP(-2*X)*(-25./8.+23*X/4.+
     1 3*X**2+X**3/3.)+(6./X)*(DELTA**2*(GAMMA+ALOG(X))+
     1 PDELTA**2*EI1-2*DELTA*PDELTA*EI2))
      RETURN
      END
```

APPENDIX B

ENERGY PERTURBATION IN THE HYDROGEN MOLECULE. (E +, E —, J, K, J (PRIME), K (PRIME), AND E** 2/R IN ELECTRON-VOLT)

E +	E -	Distan=R/A0	R (CM.)	J	K	Delta	Delta**2	J (Prime)	K (Prime)	E**2/R
11.920	59.795	.600	3.169E — 09	— 23.37744	— 23.77316	.944	.891	16.16083	12.68902	4.512E + 01
4.292	27.350	.800	4.226E — 09	— 21.54324	— 21.89680	.905	.818	15.63081	13.34121	3.384E + 01
.097	19.084	1.000	5.282E — 09	— 19.74547	— 19.91953	.858	.737	15.01281	11.82166	2.707E + 01
—1.949	13.726	1.200	6.338E — 09	— 18.05846	— 17.93961	.807	.652	14.33754	10.26078	2.256E + 01
—2.856	10.047	1.400	7.395E — 09	— 16.51589	— 16.02295	.753	.567	13.63205	8.75261	1.934E + 01
—3.133	7.442	1.600	8.451E — 09	— 15.12760	— 14.21169	.697	.486	12.91861	7.35202	1.692E + 01
—3.061	5.555	1.800	9.508E — 09	— 13.89009	— 12.53059	.641	.411	12.21456	6.09153	1.504E + 01
—2.803	4.168	2.000	1.056E — 08	— 12.79292	— 10.99198	.586	.344	11.53259	4.98575	1.354E + 01
—2.461	3.138	2.200	1.162E — 08	— 11.82264	— 9.59944	.533	.284	10.88142	4.03613	1.231E + 01
—2.093	2.366	2.400	1.268E — 08	— 10.96496	— 8.35056	.483	.233	10.26646	3.23521	1.128E + 01
—1.737	1.785	2.600	1.373E — 08	— 10.20607	— 7.23903	.435	.189	9.69056	2.57010	1.041E + 01
—1.412	1.346	2.800	1.479E — 08	— 9.53322	— 6.25609	.390	.152	9.15462	2.02519	9.669E + 00
—1.128	1.014	3.000	1.585E — 08	— 8.93501	— 5.39163	.349	.121	8.65818	1.58401	9.054E + 00
—.888	.762	3.200	1.690E — 08	— 8.40141	— 4.63501	.310	.096	8.19981	1.23056	8.460E + 00
—.691	.572	3.400	1.796E — 08	— 7.92376	— 3.97553	.275	.076	7.77746	.95004	7.963E + 00
—.531	.428	3.600	1.902E — 08	— 7.49458	— 3.40284	.244	.059	7.38876	.72926	7.520E + 00
—.405	.320	3.800	2.007E — 08	— 7.10748	— 2.90714	.215	.046	7.03118	.55683	7.125E + 00
—.306	.238	4.000	2.113E — 08	— 6.75701	— 2.47934	.189	.036	6.70214	.42308	6.768E + 00
—.229	.177	4.200	2.218E — 08	— 6.43852	— 2.11111	.166	.028	6.39916	.32000	6.446E + 00
—.171	.131	4.400	2.324E — 08	— 6.14805	— 1.79491	.146	.021	6.11988	.24100	6.153E + 00
—.126	.096	4.600	2.430E — 08	— 5.88220	— 1.52397	.127	.016	5.86209	.18079	5.886E + 00
—.093	.071	4.800	2.535E — 08	— 5.63809	— 1.29228	.111	.012	5.62376	.13512	5.640E + 00
—.068	.052	5.000	2.641E — 08	— 5.41322	— 1.09452	.097	.009	5.40302	.10063	5.415E + 00
—.050	.038	5.200	2.747E — 08	— 5.20545	— .92599	.084	.007	5.19822	.07471	5.206E + 00
—.036	.028	5.400	2.852E — 08	— 5.01295	— .78259	.073	.005	5.00782	.05529	5.014E + 00
—.026	.020	5.600	2.958E — 08	— 4.83411	— .66075	.063	.004	4.83048	.04080	4.835E + 00
—.019	.015	5.800	3.064E — 08	— 4.66755	— .55737	.055	.003	4.66498	.03002	4.668E + 00
—.014	.011	6.000	3.169E — 08	— 4.51205	— .46976	.047	.002	4.51024	.02204	4.512E + 00