

The hydrogen molecule ion in the old quantum theory

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The ground state of the H_2^+ molecule is studied using the equations of classical mechanics and the Einstein quantum condition, $J_\zeta + J_\mu = h$, where J_ζ and J_μ are the action integrals over a complete cycle of the elliptic coordinates. Strong bonding is found, but the quantitative results are good only for $R < 0.05$ and $R > 4a_0$. The greatest error comes at R_{eq} and results from the coalescence of two classically allowed regions where the electron can exist.

Key words: Old quantum theory—Bohr–Sommerfeld theory—Quantum condition.

1. Introduction

In spite of the undoubted superiority of wave mechanics, there is still considerable interest in applying classical and semiclassical methods to atomic and molecular systems. There are two valid reasons for this: one is to obtain a clearer understanding of the relationship between classical and quantum mechanics; the other is to find reasonably accurate models that are more easily solved than exact quantum mechanical treatments. In this spirit the present work deals with the hydrogen molecule ion, H_2^+ , using the method of the old quantum mechanics [1].

Recently it was shown that the old quantum theory gives remarkably good energies for two and three electron atoms [2]. An innovation was introduced in that the definite classical orbits of Bohr and Sommerfeld were replaced by probability distribution functions for the electrons, in keeping with the Uncertainty Principle. However the distribution function comes entirely from the classical equations of motion. Bohr's original quantum condition was used in the form

$$-E = \langle T \rangle = \frac{nh\nu}{2}. \quad (1)$$

However this was interpreted as an expression of the De Broglie wavelength relationship with $\langle T \rangle = v\hbar/2\lambda$, where v/ν is a path length, l , for the periodic motion, equal to $n\lambda$.

It is of great interest to see if a similar treatment can be extended to diatomic molecules. The hydrogen molecule ion is, of course, the prototype of such molecules. If it cannot be solved, then chemical bonding is not understandable in terms of the old quantum theory. Actually Bohr did attempt the solution of the hydrogen molecule with rather mediocre results [3]. However his model is not an appropriate one since the electrons were placed in a definite orbit with angular momentum about the internuclear axis.

The Bohr model was applied in a more realistic fashion to H_2^+ by W. Pauli, in his doctoral dissertation [4]. The results were very poor, since no bonding was found. Pauli used confocal elliptic coordinates,

$$\zeta = \frac{r_A + r_B}{R}; \quad \mu = \frac{r_A - r_B}{R}; \quad \phi$$

which allows the classical Hamiltonian to be separated. However the Sommerfeld quantum condition was used for each action integral, J .

$$J_\zeta = \oint p_\zeta d\zeta = \hbar = \oint p_\mu d\mu = J_\mu. \quad (2)$$

This quantum condition is notoriously unreliable, even for the hydrogen atom.

2. The classical treatment

Pauli found the classical distribution function for the electron,

$$\rho = \frac{N}{p_\zeta(\zeta^2 - 1)p_\mu(1 - \mu^2)}; \quad \int \rho d\tau = 1 \quad (3)$$

His procedure is rather lengthy. Eq. (3) can be quickly derived from a JWKB manipulation of the separated quantum mechanical Hamiltonian, retaining only the classical term. Considering only the states where $p_\phi = 0$, the classical momenta are given by

$$p_\zeta = \left(\frac{2R}{B}\right)^{1/2} \left(\frac{B\zeta - \zeta^2 - C}{\zeta^2 - 1}\right)^{1/2} \quad (4)$$

$$p_\mu = \left(\frac{2R}{B}\right)^{1/2} \left(\frac{\mu^2 + C}{1 - \mu}\right)^{1/2} \quad (5)$$

where $B = -4/RE_{el}$ and C is a separation constant. In Eqs. (4) and (5), and henceforth, atomic units are used, so that $e = m = a_0 = 1$, and $\hbar = 2\pi$.

The constant C is related to a constant of the motion found for two attracting centers and first pointed out by Hill and Erickson [5]. Using their results, C

becomes

$$C = -1 - \frac{2L_A \cdot L_B}{E_{el}R^2} - \frac{2(\cos \theta_A - \cos \theta_B)}{E_{el}R} \quad (6)$$

where $L_A(L_B)$ is the angular momentum vector of the electron about nucleus $A(B)$, and $\theta_A(\theta_B)$ is the angle between the vector $r_A(r_B)$ and the positive z axis. When R is sufficiently large, C is approximately -1 . As R approaches zero, C becomes positive. At $R = 0$, $L_A \cdot L_B = l(l+1)$ and C is positive infinity.

The values for p_ζ and p_μ determine the motions of the electron. The orbits are contained within the boundaries generated by the positive values of p_ζ and p_μ . Strand and Reinhardt have given a semiclassical treatment of H_2^+ (JWKB method) [6]. Their paper includes figures of a number of the possible classical orbits.

For the ground state of H_2^+ , Fig. 1 shows the two possible solutions. Fig. 1a is for the case where C is positive. Then μ goes from $+1$ to -1 (complete range), and ζ from $+1$ to ζ_0 , where

$$\zeta_0 = \frac{B \pm (B^2 - 4C)^{1/2}}{2}. \quad (7)$$

Fig. 1b shows the case where C is negative. Then μ ranges from ± 1 to $\pm\sqrt{-C}$, while ζ has the same range as before. The possible orbits fill up the shaded areas of the figures. The distribution function, ρ , in Eq. (3) gives the probability of finding the electron at any point ζ, μ . Since it is independent of the angle ϕ , the distribution is axially symmetric.

Fig. 1a describes the situation when the two nuclei are close together. It clearly has a strong resemblance to the square of the bonding $1\sigma_g$ molecular orbital of H_2^+ . Fig. 1b superficially resembles an anti-bonding electron distribution, since the electron density at the mid-point is zero. However it still is a bonding distribution corresponding to $1\sigma_g$ when the nuclei are far apart. Classically the electron would be trapped in one of the shaded areas only, through the distribution function, ρ , would be symmetric as shown. For classical orbits corresponding to higher states of H_2^+ , reference should be made to Strand and Reinhardt [6], or to Born [7]. The analogies to the corresponding molecular orbitals are very striking.

Eq. (3) can be used to find the average value of various properties of H_2^+ , e.g.

$$H = \frac{1}{(\zeta^2 - \mu^2)} \left[\frac{2}{R^2} [(\zeta^2 - 1)p_\zeta^2 + (1 - \mu^2)p_\mu^2] - \frac{4\zeta}{R} \right] \quad (8)$$

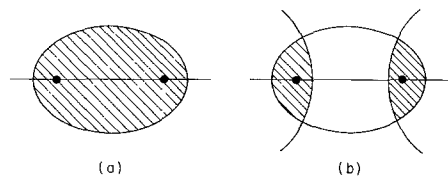


Fig. 1. Classical orbits for ground state of H_2^+ (a) when C is positive; (b) when C is negative. Electron is constrained to be in shaded areas

$$\dot{\zeta} = \frac{4p_{\zeta}}{R^2} \left(\frac{\zeta^2 - 1}{\zeta^2 - \mu^2} \right); \quad \dot{\mu} = \frac{4p_{\mu}}{R^2} \left(\frac{1 - \mu^2}{\zeta^2 - \mu^2} \right). \quad (9)$$

The mean frequencies can also be found

$$\nu_{\zeta} = \frac{\langle \dot{\zeta} \rangle}{2(\zeta_0 - 1)}; \quad \nu_{\mu} = \frac{\langle \dot{\mu} \rangle}{2(\Delta\mu)}. \quad (10)$$

The factor of two comes in because a complete cycle must be taken. The range of $\Delta\mu$ is +1 to -1 or +1 to $\sqrt{-C}$, depending on C being positive or negative. It will be shown that ν_{ζ} is usually not equal to ν_{μ} , nor simply related. This accounts for the orbits not being simple ellipses or figure eights, and why the orbits fill up the shaded areas of Fig. 1. The situation in atoms is quite different, since $\nu_r = \nu_{\theta} = \nu_{\phi}$ [2].

3. The quantum condition

So far the treatment is classical and any values of E_{cl} are possible, within reason. Quantum conditions must now be introduced to give definite energies, as well as a discrete number of states for $p_{\phi} = 0$. The quantum condition (1) is not immediately applicable because the proper value of ν is not obvious. The temptation is to write

$$\langle T \rangle = \frac{h\nu_{\zeta}}{2} + \frac{h\nu_{\mu}}{2} \quad (11)$$

but this would be correct only if the frequencies were independent. The two frequencies, while different, are not independent, being linked by the common values of B and C .

As stated earlier, the assumed basis for Eq. (1) is the De Broglie wavelength relation, $\lambda = h/mv$. To see how this is used when there are two different but dependent frequencies, consider the general case of two orthogonal coordinates, A and B , with velocities v_A and v_B and path lengths l_A and l_B for a complete cycle in each coordinate. Also let J_A and J_B be the action integrals over these cycles. Classically [7] the mean kinetic energy can be written as

$$\langle T \rangle = \frac{J_A v_A + J_B v_B}{2} \left(= \frac{nh\nu}{2} \right) \quad (12)$$

where $\nu_A = v_A/l_A$ and $\nu_B = v_B/l_B$. If $\nu_A = \nu_B$, then it is logical to assume $\nu = \nu_A = \nu_B$. This gives rise to the Einstein quantum condition [8].

$$J_A + J_B = nh = \sum_q J_q \quad (13)$$

This is obviously the correct condition to use in the atomic case,

$$\sum_q J_q = [(n-k) + (k-m) + m]h = nh \quad (14)$$

where k can have the non-integral value of $\sqrt{l(l+1)}$. Note that Eq. (14) is valid

for the ground state of H , where $n = 1$ and $k = m = 0$. The orbit is a degenerate line ellipse.

Introducing the De Broglie relation, so that $v_A^2 = h\nu_A/\lambda_A$ and $v_B^2 = h\nu_B/\lambda_B$, it is found that

$$\frac{l_A}{\lambda_A} + \frac{l_B}{\lambda_B} = n. \quad (15)$$

Assuming that this relation is valid, even if $\nu_A \neq \nu_B$, we find using Eq. (12) that Eq. (13) is regenerated. The mean frequency is simply

$$\nu = \frac{J_A\nu_A + J_B\nu_B}{nh} = \frac{J_A\nu_A + J_B\nu_B}{J_A + J_B}. \quad (16)$$

The individual frequencies are weighted by their action integrals, which seems reasonable.

The general quantum condition, $J_A + J_B = nh$, gives only a single restriction whereas we have two constants, B and C . The virial equation can be used to give a second condition.

$$\langle V_{el} \rangle = 2E_{el} + R \left(\frac{\partial E_{el}}{\partial R} \right). \quad (17)$$

This is by no means a convenient condition, but has the advantage of not introducing any further quantum assumptions. Eq. (17) is exact for classical mechanics, as well as for quantum mechanics. The modification introduced by Slater [9], adding the term $R(\partial E_{el}/\partial R)$, is general and does not depend on quantum mechanics.

Furthermore, we know that in the limits, $R = 0$ and $R = \infty$, the last term of Eq. (17) vanishes and $\langle V_{el} \rangle = 2E_{el}$. Since the old quantum theory gives exact answers for both H and He^+ , we have secure starting and finishing points. It also turns out that at large R the term in $L_A \cdot L_B$ in Eq. (6) can be ignored so that an independent evaluation of C is possible.

Since we are mainly interested in knowing whether the old quantum theory gives results that are reasonably accurate, we can also take advantage of the known, exact values for the ground state of H_2^+ to use as guidelines. In particular, the exact values of $\langle V_{el} \rangle$, as well as E_{el} , are known from the calculations of Wind [10].

4. Calculations

To make calculations, it is necessary to evaluate five integrals.

$$I_1 = \int_1^{\xi_0} \frac{\xi^2 d\xi}{(B\xi - \xi^2 - C)^{1/2}(\xi^2 - 1)^{1/2}}$$

$$I_2 = \int_1^{\xi_0} \frac{\xi d\xi}{(B\xi - \xi^2 - C)^{1/2}(\xi^2 - 1)^{1/2}}; \quad I_3 = \int_1^{\xi_0} \frac{d\xi}{(B\xi - \xi^2 - C)^{1/2}(\xi^2 - 1)^{1/2}}$$

$$I_4 = \int_{0, \sqrt{-c}}^1 \frac{d\mu}{(\mu^2 + C)^{1/2}(1 - \mu^2)^{1/2}}; \quad I_5 = \int_{0, \sqrt{-c}}^1 \frac{\mu^2 d\mu}{(\mu^2 + C)^{1/2}(1 - \mu^2)^{1/2}}.$$

These integrals can be evaluated in terms of elliptic integrals of the first, second and third kinds [6]. For positive C it is found that

$$I_4 = K/(1+C)^{1/2}; \quad I_5 = E(1+C)^{1/2} - KC/(1+C)^{1/2}$$

where K and E are complete elliptic integrals of the first and second kinds of the modulus $(1+C)^{-1/2}$. For negative C ,

$$I_4 = K; \quad I_5 = E$$

where the modulus is $(1+C)^{1/2}$. For all values of C ,

$$I_3 = \left(\frac{2}{X}\right)^{1/2} K, \text{ mod} = \left[\frac{(\zeta_0 - 1)(\zeta_0 + 1 - X)}{2X}\right]^{1/2}$$

where $X = (B^2 - 4C)^{1/2}$. The expressions for I_1 and I_2 are so complicated that it is easier to evaluate them by Gaussian quadrature.

The value of $\langle V_{el} \rangle$ is found using Eq. (3).

$$\begin{aligned} \langle V_{el} \rangle &= \frac{-N}{R} \int \int \frac{4\xi d\xi d\mu}{(B\xi - \xi^2 - C)^{1/2}(\xi^2 - 1)^{1/2}(\mu^2 + C)^{1/2}(1 - \mu^2)^{1/2}} \\ &= \frac{-4I_2 I_4}{R(I_1 I_4 - I_3 I_5)} = \frac{BE_{el} I_2 I_4}{(I_1 I_4 - I_3 I_5)}. \end{aligned} \quad (18)$$

The normalization constant is $(I_1 I_4 - I_3 I_5)^{-1}$.

The action integrals are found to be

$$\begin{aligned} J_\xi &= R(-2E_{el})^{1/2}(BI_2 - CI_3 - I_1) \\ J_\mu &= R(-2E_{el})^{1/2}(CI_4 + I_5)(f) \end{aligned} \quad (19)$$

where the factor f is two for J_μ when C is positive. Otherwise the factor is one. The frequencies are

$$\nu_\xi = \frac{(-2E_{el})^{1/2} I_4}{R(I_1 I_4 - I_3 I_5)}; \quad \nu_\mu = \frac{(-2E_{el})^{1/2} I_3}{R(I_1 I_4 - I_3 I_5)(f)} \quad (20)$$

where again the factor of two is used in the denominator for ν_μ when C is positive, and one otherwise.

An equation for the energy can be written in the convenient form

$$-E_{el} = \frac{h^2}{2R^2(J'_\xi + fJ'_\mu)^2} \quad (21)$$

where $J'_\xi = BI_2 - CI_3 - I_1$, and $J'_\mu = CI_4 + I_5$.

At $R=0$ it is more convenient to evaluate the action integrals directly. Since $\xi \rightarrow 2r/R$ and $\mu \rightarrow \cos \theta$, only J_ξ contributes and $J_\mu = 0$. If C is no larger than

$1/R$, than J_ζ becomes identical with J_r for He^+ in its ground state. That is, $J_\zeta = h$ and $-E_{el} = 2.00$ a.u.

At $R = \infty$, the value of C can be found from Eq. (6). If the electron is on nucleus A , then $\langle \cos \theta_A \rangle = 0$ and $\langle -\cos \theta_B \rangle = 1$, or $C = -1 + B/2$. The values of $I_4 = \pi/2 + \pi B/16$, $I_5 = \pi/2 - \pi B/16$ and $I_3 = \pi/2 + \pi B/16$ can now be found by an expansion of the complete elliptic integrals when the modulus is small. Also I_1 and I_2 may be estimated from $I_1 = I_2(\zeta_0 + 1)/2$ and $I_2 = I_3(\zeta_0 + 1)/2$, where $\zeta_0 = 1 + B/4$. This gives $I_1 = \pi/2 + 3\pi B/16$ and $I_2 = \pi/2 + \pi B/8$. These values give $\nu_\zeta = \nu_\mu$ and $J_\zeta = J_\mu = h/2$. The frequency is the same as that of the hydrogen atom and $\langle T \rangle = 0.500$ a.u.. The potential energy is $-1.00 - 1/R$ and $-E_{el} = 0.500 + 1/R$, the correct value at this level.

These results in the limits may be compared to those obtained using the quantization procedure for H_2^+ in the JWKB method [6]. With the Keller and Maslov rules [11], the quantum conditions are found to be $J_\zeta = J_\mu = h/2$, for all values of R . This agrees with the above result at $R = \infty$. However at $R = 0$, it is definitely wrong since the JWKB method for hydrogenic atoms gives the right energy only if there is a false orbital angular momentum with $(l + 1/2)^2$ replacing $l(l + 1)$ [12]. The assumption that C is no greater than $1/R$ allows the calculation that $J_\mu = 0$. The basis for this is easily seen by examining Eq. (6). The results given below will justify the assumption.

To make calculations at other values of R , it is most convenient to pick a value of B corresponding to some exact value of R and E_{el} . Then C is varied until Eq. (17) is satisfied in the form

$$\Delta = -\frac{R}{E_{el}} \left(\frac{\partial E_{el}}{\partial R} \right) = \frac{-BI_2 I_4}{I_1 I_4 - I_3 I_5} + 2 \quad (22)$$

where Δ is the exact value from the literature [10].

Table 1 shows the results of such calculations for a number of different values of B . The calculated values of C can now be checked using Eq. (6).

The separate components for C can be found from the distribution function.

$$\left\langle \frac{-2(\cos \theta_A - \cos \theta_B)}{E_{el} R} \right\rangle = \frac{V_{el}}{E_{el}} \left(\frac{I_4 - I_5}{I_4} \right) \quad (23)$$

$$\left\langle \frac{-2L_A \cdot L_B}{E_{el} R^2} \right\rangle = C + 1 - \frac{V_{el}}{E_{el}} \left(\frac{I_4 - I_5}{I_4} \right). \quad (24)$$

Setting the left hand side of Eq. (24) equal to zero gives an equation which is satisfied only by a definite value of C for each value of B .

When this equation is solved by iteration, it is found that the same value of C is calculated as in Table 1, providing R is greater than about $4a_0$. For $R = 3.00 a_0$, C is calculated as -0.092 , and for $R = 2.00$, C is calculated as $+0.050$, and it is no longer safe to ignore the left hand side of Eq. (24). Calculation of $\langle L_A \cdot L_B \rangle$ from (24), using the C values from Table 1, shows that it is small, but not zero.

Table 1. Parameters for H_2^+ as a function of R by old quantum theory

R	B^a	C^b	Δ^c	$J_\zeta + J_\mu$
0.000	∞	∞	0.000	1.000 h
0.050	40.12	22.00	0.011	1.037
0.100	20.22	9.70	0.019	1.061
0.500	4.611	0.950	0.187	1.129
1.00	2.755	0.183	0.330	1.209
1.50	2.135	0.085	0.410	1.330
2.00	1.814	0.038	0.454	1.436
3.00	1.464	-0.044	0.479	0.960
4.00	1.256	-0.097	0.450	0.995
6.00	0.9824	-0.197	0.323	1.018
7.00	0.8811	-0.320	0.267	1.010
10.00	0.6660	-0.558	0.173	1.004
12.50	0.5516	-0.740	0.139	1.000
∞	0.000	-1.000	0.000	1.000

^a $B = -4/RE_{el}$.

^b Calculated to give exact value of Δ .

^c $-\Delta = R/E_{el}(\delta E/\delta R)$ from Ref. [10].

The values of $\langle L_A \cdot L_B \rangle$ are not quantized, nor are they expected to be since this orbital angular momentum is strongly quenched.

The next step is the calculation of J_ζ and J_μ , using equation (19). Again, for convenience, the exact values of R and E_{el} are used for each value of B . Table 1 shows the sum, $J_\zeta + J_\mu$, calculated in this way. If this sum is equal to h , then the quantum condition (13) is valid, and the exact E_{el} could be calculated from Eq. (21). It can be seen that for negative C , $J_\zeta + J_\mu \cong h$, but that for positive C , the agreement is very poor for $R > 0.05 a_0$.

5. Discussion

The failure that is found when C becomes positive is not unexpected. At this point the two classical orbits coalesce, as shown in Fig. 1. This causes a catastrophe in the quantum conditions, since suddenly the frequency ν_μ is halved, or conversely J_μ is doubled. This is an artificial effect since obviously both in wave mechanics and in classical mechanics, no dramatic change would occur near $C = 0$. As R approaches zero, the discrepancy should disappear, as shown in the Table. However it is somewhat surprising that even at $R = 0.05$, $J_\zeta + J_\mu$ has not approached h more closely.

In semi-classical theory there is a remedy for avoiding the catastrophe due to a doubling of the allowed coordinate [13–15]. This is to include a quantum mechanical correction for tunnelling through a potential energy barrier, as in Fig. 1b, and a correction for reflection from the top of the barrier, as in Fig. 1a. Then the factor f changes smoothly from 1 to 2 over a range of R values. If ω

is the transmission coefficient,

$$f = 1 + \omega = 1 + (1 + e^{-2\pi\epsilon})^{-1} \quad (25)$$

where ϵ depends on the shape of the barrier.

When $C = 0$, $\epsilon = 0$ and $\omega = 1/2$. When $R = 2.00$ or 3.00 in Table 1, J'_ζ and J'_μ are of comparable magnitude. Therefore the tunnelling correction at $R = 3.00$ will be too large, and the reflection correction at 2.00 will be too small, though in the right direction. The improvement in the value of $(J'_\zeta + J'_\mu)$ at $R = 2.00$ will be more than offset by a worsening at $R = 3.00$.

While tunnelling does not seem to be a useful correction, it might still be possible to derive or invent a quantum condition that gives better results. Still the anomaly at $C = 0$ cannot be entirely avoided. For example, I_4 becomes infinite at $C = 0$. From Eq. (22) we see that

$$\Delta = -\frac{BI_2}{I_1} + 2 \cong \frac{2}{B+1}. \quad (26)$$

If C becomes zero between $R = 2.00$ and 3.00 , as Table 1 suggests, then $\Delta \cong 0.72$. But this is much larger than the exact values for Δ in this range ($\Delta \cong 0.46$).

Thus a plot of E_{el} vs. R will show a break, or *glitch*, in this region. For small negative values of C , the energy will be too positive, and for small positive values of C , the energy will be too negative. The alternative would be for a plot of C vs. R to be discontinuous, with $C = 0$ an excluded value.

In view of the difficulties discussed above, it must be concluded that the old quantum theory is not useful for quantitative discussion of chemical bonding. It is a frustrating, and interesting, fact that the difficulties are most severe in the region of R_{eq} , of greatest importance in bonding. Still it must be noted that the old quantum theory does *predict* the existence of the chemical bond. Even with the inadequate quantum conditions available, it is clear that a hydrogen atom will strongly bond to a proton. It is also noteworthy that the old quantum theory works well at values of R greater than about $4a_0$.

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