

Charge cloud study of atomic and molecular structure

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The conceptually simple charge cloud model of atomic and molecular structure is applied to three problems: atomic hydrogen, molecular hydrogen, and crystalline lithium hydride. Because of its simplicity, the model lends itself well to calculations that are easily performed by undergraduates. While the calculations are, on the whole, only in modest agreement with experimental results, the model provides useful insights in all the areas to which it is applied.

INTRODUCTION

During the early 1950s George Kimball and his students Neumark¹ and Kleiss² investigated an interesting model of atomic and molecular structure that has become known as the charge cloud model of atomic and molecular structure. One of the motivations for this study apparently was the fact that, at that time, quantum-mechanical studies of simple molecular systems more complicated than molecular hydrogen were not yielding fruitful results because of the complexity of the calculations.

The subsequent development of high-speed computers solved many difficulties, and interest in the charge cloud model from a research perspective dwindled. The model, however, has certain attractive features which make it a valuable pedagogical tool in undergraduate physics and chemistry courses. This paper presents applications of the charge cloud model to simple atomic, molecular, and crystalline systems.

ATOMIC STRUCTURE—THE HYDROGEN ATOM

The charge cloud model of atomic hydrogen is given in Fig. 1. It consists of a point charge nucleus surrounded by an electron charge cloud of radius R and even charge distribution throughout. The charge density, $\rho(r)$, is $-q(4/3\pi R^3)^{-1}$ at any point within the sphere. The calculation of the hydrogen atom energy levels is a simple task on the basis of this model.

Kinetic energy

Quantization of kinetic energy is a direct manifestation of de Broglie's hypothesis that matter has wave-like properties and that the wavelength of an electron, for instance, is inversely proportional to its momentum, $\lambda = h/mv$. The kinetic energy of a spherical electron charge cloud (see the Appendix) is inversely proportional to the square of the cloud radius:

$$T = 9n^2/8R^2 \quad (\text{in atomic units}). \quad (1)$$

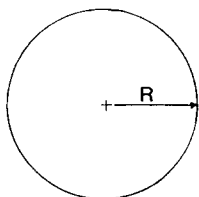


Fig. 1. Charge cloud model of atomic hydrogen.

Potential energy

The electric potential³ at any point, r , from the center of a spherical charge cloud of radius R (and uniform charge density) is

$$\phi(r) = -(q/2)(3/R - r^2/R^3). \quad (2)$$

Therefore, at the center of the charge cloud ($r = 0$) we have

$$\phi(r) = -3q/2R \quad (3)$$

and, thus, a potential energy interaction between the charge cloud and the nucleus of

$$V = \phi(0)q = -3/2R \text{ a. u.} \quad (4)$$

Total energy

The total energy of the hydrogen atom,

$$E_H = 9n^2/8R^2 - 3/2R, \quad (5)$$

is plotted (for the ground state, $n = 1$) along with the potential energy and kinetic energy in Fig. 2.

Minimization of E_H with respect to the charge cloud radius yields the equilibrium radius, $R = 1.5n^2$, which

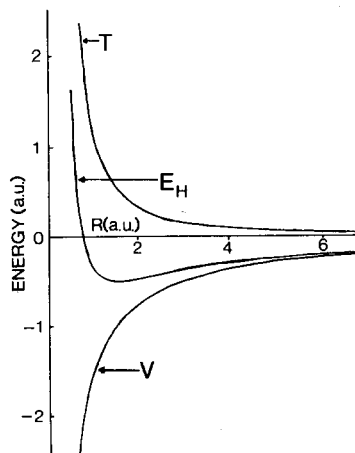


Fig. 2. Results of charge cloud analysis of atomic hydrogen.

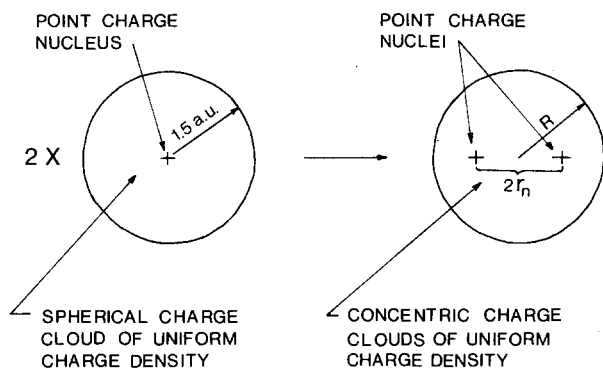


Fig. 3. Formation of molecular hydrogen on the basis of the charge cloud model.

when substituted into Eq. (5) gives the energy of the ground and excited states of the hydrogen atom:

$$E_H = -0.5/n^2 \text{ a. u.} = -13.6/n^2 \text{ eV.} \quad (6)$$

In addition to yielding the correct energy levels for atomic hydrogen, the charge cloud model provides a clear picture of atomic stability. The stability of atoms is a direct consequence of the wave nature of matter as hypothesized by de Broglie. Atoms do not collapse under nuclear attractive forces because, as the electron cloud decreases in size, the kinetic energy approaches positive infinity faster than the potential energy approaches negative infinity.

COVALENT BONDING—THE HYDROGEN MOLECULE

The charge cloud picture of the formation of molecular hydrogen is shown in Fig. 3. Again, this simple model lends itself well to undergraduate-type calculations. The contributions to the internal energy of the hydrogen molecule are (i) electron kinetic energy, (ii) electron-electron repulsion, (iii) nuclear-nuclear repulsion, and (iv) electron-nuclear attractions. Only the last contribution is negative and, therefore, is responsible for stable molecule formation.

Electron kinetic energy

For two interpenetrating, concentric charge clouds of radius R , the kinetic energy is

$$T = 2(9/8R^2) \text{ (ground state).} \quad (7)$$

Electron-electron repulsion

This potential energy term involves the evaluation of the following integral:

$$V_1 = \int_0^R \phi(r)\rho(r)4\pi r^2 dr. \quad (8)$$

Starting at the center of the charge cloud, the electric potential at r due to one of the electron clouds, $\phi(r)$, is multiplied by the amount of charge due to the other electron at r , $\rho(r)4\pi r^2 dr$. This is done for all spherical volume elements within the sphere. Substitution of Eq. (2) and

the value for $\rho(r)$ into Eq. (8) yields

$$V_1 = 6/5R \text{ a. u.} \quad (9)$$

Nuclear-nuclear repulsion

In Fig. 3 it is assumed that the nuclei are symmetrically arranged about the center of the electron charge cloud at a separation of $2r_n$. Therefore,

$$V_2 = 1/2r_n \text{ a. u.} \quad (10)$$

Electron-nuclear attraction

Since the nuclei are symmetrically arranged at a distance r_n from the center of the two-electron charge cloud, the potential energy of this interaction is

$$V_3 = 4\phi(r)(+q). \quad (11)$$

The factor 4 takes into account that there are a total of four electron-nuclear interactions. Substitution of the expression for $\phi(r)$ yields

$$V_3 = -6/R + 2r_n^2/R^3. \quad (12)$$

Since $r_n < R$, the first term on the right-hand side of Eq. (12) will predominate and V_3 will be favored by small values of R , whereas the other three contributions to the total energy are favored by large charge clouds. The charge cloud model clearly shows that it is the attraction of the two nuclei for the same electron charge cloud that results in a stable chemical bond.

Total energy

The total internal energy of the hydrogen molecule is

$$E_{H_2} = 9/4R^2 - 24/5R + 2r_n^2/R^3 + 1/2r_n. \quad (13)$$

Minimization of the total energy with respect to R and r_n yields

$$R = 2r_n = 15/11 \text{ a. u.},$$

which, when substituted into Eq. (13), gives the ground state energy of the hydrogen molecule,

$$E_{H_2} = -1.21 \text{ a. u.}$$

Bond energy and bond length

This result cannot be tested directly because the total energy of the hydrogen molecule cannot be measured experimentally. However, the bond energy of H_2 , the energy change accompanying the process



has been measured. The charge cloud model yields the

Table I. Summary of charge cloud calculation for the bond energy of H_2 .

H ₂		2H	
$T = 1.21$	$T = 1.0$	$\Delta T = -0.21$	
$V_1 = 0.73$			
$V_2 = 0.88$	$V = -2.0$	$\Delta V = 0.42$	
$V_3 = -4.03$			
$E_{H_2} = -1.21$	$2E_H = -1.0$	$\Delta E = -0.21$	

following value for the bond energy of H_2 :

$$\begin{aligned} \text{bond energy} &= 2E_H - E_{H_2} \\ &= 2(-0.5 \text{ a. u.}) - (-1.21 \text{ a. u.}) \\ &= 0.21 \text{ a. u.} = 5.71 \text{ eV.} \end{aligned}$$

Given the simplicity of the model, this is fairly good agreement with the experimental value of 4.75 eV.⁴ Another experimentally verifiable quantity is the bond length. The calculated value $2r_n$ or 15/11 a.u. or 0.72 Å also compares favorably with the literature value of 0.74 Å.

Table I summarizes the charge cloud calculation for the bond energy of H_2 . It is important to note that the virial theorem ($E = -T = V/2$) is satisfied for the calculation of the total energy of both atomic and molecular hydrogen. It is, therefore, also satisfied for the bond-breaking process represented by Eq. (14).

IONIC BONDING—LiH(s)

Lithium hydride is a white solid which crystallizes with the face-centered cubic lattice structure. The lattice energy of LiH is the energy change accompanying the following (hypothetical) process:



In this section the charge cloud model will be used to calculate the lattice energy of LiH. This will be accomplished by first calculating the gas-phase energies of the ions on the left-hand side of Eq. (15), and then subtracting them from the charge cloud calculation for the internal energy of LiH(s). For this calculation we will assume the face-centered lattice structure for LiH(s).

Li⁺(g) and H⁻(g)

The internal energies of the spherical, two-electron ions, $Li^+(g)$ and $H^-(g)$, are easily calculated by the methods outlined earlier:

$$E_+(g) = 9/4R_+^2 - 39/5R_+, \quad (16)$$

$$E_-(g) = 9/4R_-^2 - 9/5R_-, \quad (17)$$

where the first term on the right-hand sides equal T and the second term equals $V_1 + V_3$. Minimization of the in-

Table II. Energies of gas-phase ions.

Ion	Radius	Energy
$Li^+(g)$	0.577 a.u.	-6.758 a.u.
$H^-(g)$	2.500 a.u.	-0.360 a.u.
		-7.118 a.u.

ternal energies of $E_+(g)$ and $E_-(g)$ with respect to the charge cloud radii, R_+ and R_- , yields the data in Table II.

LiH(s)

The internal energy of crystalline LiH consists of three contributions: the internal energy of the Li^+ ion, the internal energy of the H^- ion, and the Coulombic interaction energy of the ions in the lattice.

$$E_{LiH} = E_+ + E_- + E_{Coul}. \quad (18)$$

For a face-centered cubic lattice (Fig. 4), E_{Coul} consists of the electrostatic interactions between a Li^+ ion and its 6 nearest neighbor H^- ions at a distance R_\pm , its 12 next-nearest neighbor Li^+ ions at a distance of $\sqrt{2}R_\pm$, its 8 next-next-nearest neighbor H^- ions at a distance of $\sqrt{5}R_\pm$, and so on. Thus,

$$\begin{aligned} E_{Coul} &= (-6/R_\pm + 12/\sqrt{2}R_\pm - 8/\sqrt{5}R_\pm + \dots) \\ &= -1.748/\sqrt{2}R_\pm, \end{aligned} \quad (19)$$

where R_\pm is the sum of the ionic radii ($R_+ + R_-$) and 1.748 is the Madelung constant⁵ for the face-centered cubic lattice structure. If the ratio R_+/R_- is less than 0.414,⁶ the cations "rattle" in the octahedral holes created by the anions. It is not difficult to show that, under these circumstances,

$$E_{Coul} = (-6\sqrt{2}R_- + 12/2R_- - 8/\sqrt{10}R_- + \dots)$$

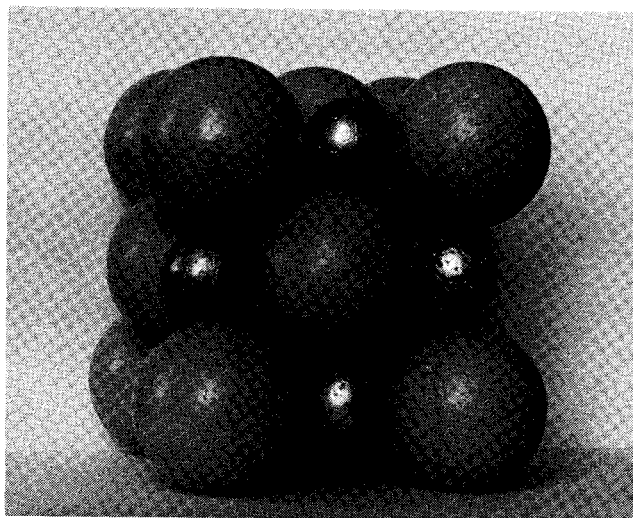


Fig. 4. Charge cloud model of face-centered cubic LiH. The small spheres represent the lithium ions, and the large spheres represent the hydride ions.

$$= -1.748/\sqrt{2}R_- \quad (20)$$

The total energy of LiH(s) can therefore be written as

$$E_{\text{LiH}} = 9/4R_+^2 - 39/5R_+ + 9/4R_-^2 - 9/5R_- + E_{\text{Coul}}, \quad (21)$$

where

$$E_{\text{Coul}} = -1.748/R_+ \quad \text{for } R_+/R_- \geq 0.414, \\ = -1.748/\sqrt{2}R_- \quad \text{for } R_+/R_- < 0.414.$$

The minimum energy for LiH(s) is now found analytically by varying R_+ and R_- . The results of this minimization process yield $E_{\text{LiH}} = -7.78$ a.u. with $R_+ = 0.58$ a.u. and $R_- = 1.48$ a.u.

Lattice energy

The lattice energy, U , for LiH(s) is calculated to be

$$U = E_{\text{LiH}} - E_+(g) - E_-(g) \\ = -7.78 \text{ a.u.} - (-6.758 \text{ a.u.}) - (-0.360 \text{ a.u.}) \\ = -0.66 \text{ a.u.} = -413 \text{ kcal/mole.}$$

This value is larger than the literature value of -218 kcal/mole⁷ by about a factor of 2. Again, this is not a bad comparison given the simplicity of the model. The charge cloud model gives a rather succinct picture of ionic bonding. There are only two adjustable parameters, R_+ and R_- , and they both have very clear physical significance.

CONCLUSION

Because of its conceptual simplicity, the charge cloud model provides valuable insights into atomic stability, chemical bond formation, and ionic interactions in crystals. Working with the model can provide students with direct exposure to the fundamentals of quantum theory and much useful practice with electrostatic calculations.

The calculations discussed in this paper could serve as challenging problem assignments for undergraduates. Additional problems of interest are calculation of the ioniza-

tion energy of He and Li, calculation of the bond energy of H_2^+ , calculation of the ground-state energy of positronium, and calculation of the lattice energy of BeH_2 .

APPENDIX: KINETIC ENERGY OF A SPHERICAL ELECTRON CHARGE CLOUD

Neumark¹ employed the uncertainty principle in a rigorous derivation of Eq. (1). (See also a recent article in this Journal by Wolsky.⁸) For the benefit of undergraduates, however, it may be desirable to sacrifice some rigor in the interest of an explicit discussion of the quantization of kinetic energy and its $1/R^2$ dependence.

In an alternative derivation, de Broglie's wave equation, $\lambda = h/mv$, is used. It is stressed that, because of the electron's wave nature, it is subject to interference phenomena. In a spherical charge cloud of radius R , standing waves of half-integral wavelength must fit within the diameter of the sphere:

$$(n/2)\lambda = 2R.$$

When de Broglie's wave equation is substituted into the above equation and it is solved for the kinetic energy, one obtains

$$T = n^2\hbar^2/32mR^2,$$

which is in error by a factor of $9/\pi^2$. The correct kinetic energy expression is

$$T = 9n^2\hbar^2/32\pi^2mR^2 = 9n^2/8R^2 \text{ (a. u.)}.$$

¹G. F. Neumark, Microfilm Abstr. **11**, 834 (1951).

²L. M. Kleiss, Diss. Abstr. **14**, 1562 (1954).

³The evaluation of $\phi(r)$ provides a challenging problem assignment for students.

⁴G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, NJ, 1950).

⁵C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971).

⁶The value 0.414 is the radius ratio (R_+/R_-) for which the smaller cation just fits within the octahedral hole formed by the larger anions.

⁷J. Sherman, Chem. Rev. **11**, 93 (1932).

⁸A. M. Wolsky, Am. J. Phys. **42**, 761 (1974).