

## Search for Simplicity

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity

We shall begin with a simple problem which does not yet involve quantum mechanics. It is measuring the size of molecules. We do this by finding the distance between neighboring molecules in liquids, assuming that the molecules touch each other because of the low compressibility of liquids. Let us start with water.

Our method is as near as possible to a direct perception by our senses. We perform two measurements which are easy to visualize and to anticipate the result. One is a measurement of the surface tension. A water film extends in a rectangular wire frame of 1-cm width in a vertical plane. The lowest side of the frame can move up and down along the prolonged sides of the rectangle with a weight attached (see Fig. 1). It would not surprise anyone that about a tenth of a gram (exactly 0.145 g) is just in equilibrium with the tension of the water film. (Remember that some insects can walk on a water surface. An insect weighs about 0.01 g and spans a surface of about 0.1 cm<sup>2</sup>.) If the weight were less, the surface tension would pull it upwards; if it were more, the weight would pull it down. From this we conclude that the work necessary to increase the surface of the film by 1 cm<sup>2</sup> is about 0.1-g weight lifted 1 cm, or about 100 ergs (exactly 145 ergs). This corresponds to twice the surface tension  $S$ , since extending the film by 1 cm<sup>2</sup> creates two new surfaces of 1 cm<sup>2</sup>, one on each side.

The second measurement is heating and boiling away 1 cm<sup>3</sup> of water from room temperature, a daily experience at breakfast. How much energy is expended? Let us call it  $\epsilon_B$ . We need 80 calories to reach the boiling point and then 540 calories to evaporate it; so we get  $\epsilon_B = 620 \text{ cal} = 2.6 \times 10^{10}$  ergs. This amount of energy and the previous one are both within our immediate experiences. The ratio is  $R \equiv 2S/\epsilon_B = 5.6 \times 10^{-9}$ . The work to extend the water film by 1 cm<sup>2</sup> is about 200 million times smaller than the work to transform a gram of water into steam. That small ratio between two easily visualizable energies leads to the small molecular size, about 100 million times smaller than 1 cm.

How can we get to the distance between molecules from that ratio? Extending the film by 1 cm<sup>2</sup> creates two new surfaces of that area, as remarked before. The boiling is equivalent to removing and isolating all molecules. We can think of achieving this in our mind by the following process (a student of mine called it the "salami method"). Take an extremely sharp and thin knife and slice the cubic centimeter in slices as thin as the linear dimensions of one mole-

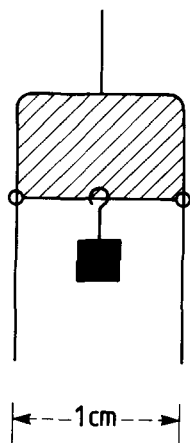


Fig. 1. A water film supporting a weight of 0.145 g.

cule. There will be  $d^{-1}$  such slices when  $d$  is the distance between molecules. The molecules are not yet isolated. Now perform again  $d^{-1}$  cuts perpendicular to the previous cuts; we then get linear strings of molecules. A third cutting in the third direction isolates all molecules (see Fig. 2) and ought to be roughly equivalent to boiling.

Each cut produces two surfaces of 1 cm<sup>2</sup>; thus it requires the same energy as extending the film by 1 cm<sup>2</sup>. Three  $d^{-1}$  cuts were necessary, so that the total binding energy must be  $\epsilon_B = 3d^{-1} \cdot 2S$  or

$$d = 3R = 6S/\epsilon_B. \quad (1)$$

With our value of  $R$  we obtain a distance  $d = 1.7 \times 10^{-8}$  cm. This value is of the right order of magnitude but somewhat too low (the actual value is  $3.16 \times 10^{-8}$ ). As we will see later on, the discrepancy can be traced to the fact that water molecules are very asymmetric with the hydrogen atoms attached to the oxygen at right angles, on one side only, as it were.

The method should work better with liquids whose constituents are more symmetric so let us apply it to cleaning fluid, CCl<sub>4</sub>, and to liquids Neon and Argon. The Cl atoms in CCl<sub>4</sub> surround the carbon atom symmetrically on the edges of a tetrahedron. In Ne and Ar the constituents are atoms with closed spherical shells. Table I gives the surface tensions  $S$ , the binding energies  $\epsilon_B$ , and the resulting distance  $d$  together with the actual value. The energy of raising the temperature to the boiling point is appreciable only in the case of water. In the other cases,  $\epsilon_B$  is practically equal to the heat of evaporation.

The surface tensions are those at 20°C for H<sub>2</sub>O and CCl<sub>4</sub>, and at -248° and -188°, respectively, for Ne and Ar. As expected, our method works quite well for liquids with symmetric constituents. Note that  $\epsilon_B$  for CCl<sub>4</sub> is less than 1/8 of that of water. This is why cleaning fluid has such a strong smell.

The physical basis of our method can be understood as follows. A molecule in the interior of the liquid is bound to its neighbors with a binding energy  $\epsilon_0$ . A molecule at the

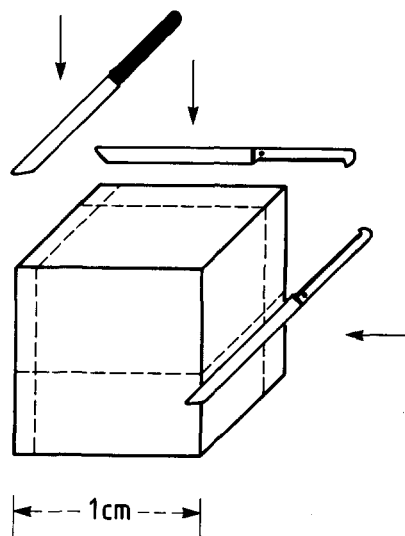


Fig. 2. The so-called "salami method" separating the molecules of a cubic centimeter of water.

Table I. Surface tension  $S$ , binding energy  $\epsilon_B$ , resulting distance  $d$ , and actual value for  $\text{H}_2\text{O}$ ,  $\text{CCl}_4$ ,  $\text{Ne}$ , and  $\text{Ar}$ .

	$\text{H}_2\text{O}$	$\text{CCl}_4$	$\text{Ne}$	$\text{Ar}$
$S$ in ergs/cm <sup>2</sup>	73	27	5.5	13.2
$\epsilon_B$ in $10^9$ ergs/cm <sup>3</sup>	26	3.1	1.1	2.7
$d$ from (1) in $10^{-8}$ cm	1.7	5.2	3.0	3.0
Actual value of $d$	3.2	5.4	3.0	3.4

surface is less bound because it has no neighbor above. We can estimate that difference by assuming that the binding is composed of six bonds in the directions up, down, right, left, forward, and backward. For a molecule at the surface, one of them is missing, so the binding energy would be about  $(5/6)\epsilon_0$ . Therefore a surface has an energy surplus (binding means negative energy). For  $1 \text{ cm}^2$  this surplus is the surface tension  $S = (1/6)\epsilon_0 d^{-2}$ , where  $d^{-2}$  is the number of molecules in  $1 \text{ cm}^2$  of the surface. The energy  $\epsilon_B$  needed to take the cubic centimeter apart into separate molecules is  $\epsilon_B = \epsilon_0 d^{-3}$ , where  $d^{-3}$  is the number of molecules in the cube. Thus we get the relation (1) for  $d$ , the same result as from our previous consideration.

The ratio  $5/6$  for the binding on the surface to the one inside is only an estimate which is a good approximation for spherical molecules. In the case of water we expect a ratio closer to unity because of the following reason. The water molecule carries a large electric dipole moment (remember the large dielectric constant of water). The bond between molecules comes from the attraction of the positive side of one molecule by the negative side of its neighbor (hydrogen bond). At the surface the molecules will arrange themselves such as to lie with their dipoles parallel and not perpendicular to the surface. Hence relatively less of the binding is lost compared to the interior, than with molecules for which the binding is spherically symmetric. Thus the surface tension is less than  $(1/6)\epsilon_0 d^{-2}$ , say  $f^{-1}\epsilon_0 d^{-2}$

with  $f > 6$ . Then expression (1) becomes  $d = fS/\epsilon_B$  leading to a larger value of  $d$ .

This is the kind of consideration which we will frequently use when our conclusions are valid only under simple conditions. We will try to understand qualitatively (not quantitatively) in what direction the result deviates when the circumstances are not as simple as assumed. The simple conditions are especially suited to bring out the physical content.

We have not yet established any connection between the quantities used here, such as  $S$  or  $\epsilon_0$ , and the fundamental constants of quantum mechanics such as the charge  $e$  and the mass  $m$  of the electron and Planck's constant  $h$ . This will be done in future essays.

There are two questions left, the first of which I know the answer; it will be provided in the next issue. I do not know the answer to the second one, and I hope that a reader may provide it.

The first question is the following. The above considerations should also apply to solids. The distance  $d$  between atoms should be given by (1) when  $2S$  is interpreted as the work necessary to perform one cut as illustrated in Fig. 2. The binding energy  $\epsilon_B$  is larger than in liquids by the melting heat; the latter, however, is only of the order of 10% of the heat of evaporation. But the effort to cut into a solid seems to be extremely much higher so that one would get much larger distances  $d$ . In fact,  $d$  is of the same order of magnitude, if not smaller. How can one resolve this discrepancy?

The second question: Applying the same method to mercury and to molten metals such as  $\text{Mg}$ ,  $\text{Fe}$ , and  $\text{Cd}$ , one obtains values of  $d$  up to three times too large. Why? This is all the more surprising because formula (1) gives smaller values than the actual ones for molten metals such as  $\text{Na}$ ,  $\text{Al}$ ,  $\text{Cu}$ ,  $\text{Ag}$ ,  $\text{Sn}$ , and  $\text{Pb}$ . The surface tension in the former metals is more than our estimate of  $(1/6)\epsilon_B d^{-2}$ . It is easy to understand lower values along similar lines as we used for water, by arguing that the surface atoms adjust themselves such that their energy is lowered, but hard to understand larger ones.

Victor F. Weisskopf

## The surface of water, or ice

G. J. Turner

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## LETTERS TO THE EDITOR

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### IS THERE A FUTURE FOR THE TACHYON?

Recent articles on Bell's theorem and the EPR paradox<sup>1</sup> seem to imply that the tachyon<sup>2</sup> may soon come into its own. The superluminal EPR interaction may be mediated virtual particles of imaginary mass, whose effective range is infinite, because they can flit up and back over arbitrary distances in no time, to exert their exotic influence on photons, or anything for that matter.

It is theoretically possible to put the earth-moon system into a coherent quantum state, such that an action on earth will immediately affect the moon. It may be that we have been holding the moon captive that way, and that it would really get queer if nobody watched (if you look away, the moon will play, so to speak).<sup>3</sup>

Virtual tachyons could be exchanged so fast that, according to the Heisenberg uncertainty principle, their energy would be completely uncertain; but, due to the great distances over which they could be exchanged, their momentum could be very certain, as indeed it would have to be, if they are to follow such a straight and narrow course over such distance. If particles of imaginary rest mass are exchanged at infinite speed, their metamass (the magnitude of the imaginary mass) must be infinite, so the energy (the ratio of two infinite quantities in this case) is indeterminate, and their momentum (which reduces to the metamass multiplied by the speed of light) will certainly be infinite. This infinite (yet virtual) momentum must carry out the deeds done in EPR experiments in such a short time that the quantum theory does not require conservation of energy or momentum; thus it is like borrowing a huge quantum of energy momentum from Mother Nature, and repaying it before she has a chance to miss it.

There is then the Fermi paradox,<sup>4</sup> regarding why it is that we are not

swamped by superluminal communications from all over the universe (and beyond). The difficulty of setting up an EPR experiment in the laboratory, however, seems to give the answer. To establish a faster-than-light communication link between remotely distant points, one would have to get the apparatus set up at both ends, with relay stations in between, so it would, in effect, be tantamount to creating a medium of refractive index less than 1, except that it would be a mysterious quantum signal (carried by tachyons rather than photons) which this medium would convey, when one collapses its wavefunction (as Davies puts it) or reduces its state vector (as Paul puts it). Instead of God playing dice with the universe, it is like people setting up God's dominoes, to knock them down at superluminal speed!

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20 June 1985

<sup>1</sup>H. P. Stapp, *Am. J. Phys.* **53**, 306 (1985); see, also, H. Paul, *Am. J. Phys.* **53**, 318 (1985).

<sup>2</sup>O. M. P. Bilaniuk, V. K. Deshpande, and E. C. G. Sudarshan, *Am. J. Phys.* **30**, 718 (1962); see, also, P. C. W. Davies, *The Physics of Time Asymmetry* (Univ. of California, Berkeley, 1974).

<sup>3</sup>N. D. Mermin, *Phys. Today* **38**, 38 (1985).

<sup>4</sup>T. Donaldson, *Analog Sci. Fict. Sci. Fact CV*, 77 (June 1985). The superluminal is somewhere between fact and fiction, waiting, like Schrödinger's cat, to go one way or the other. Imaginary particles, like imaginary numbers, may be an idea whose time has come.

### DEMONSTRATION TRUMPET WITH A TROMBONE

The note "Demonstration trumpet"<sup>1</sup> was of particular interest to me because I have been using a similar demonstration with a conventional trombone. I have done it in musical acoustics classes for several years now. My approach lacks some of the

simple elegance of that special demonstration trumpet. However, it works almost as well and has the advantage that you do not need to destroy an instrument to perform the experiment.

What I do is push a piece of ordinary  $\frac{1}{2}$ -in. garden hose snugly into the bell of my trombone and trim the hose flush with the end of the bell. (The actual dimensions of the scrap hose I use are  $\frac{2}{8}$ -in. i.d.,  $\frac{3}{4}$ -in. o.d., and  $19\frac{1}{4}$  in. long.) The counted frequencies of the tones blown without and with the hose are then compared and give very close to 2:3:4:5:6 and 3:5:7:9:11 ratios, respectively.

Something not mentioned in the note cited was the special technique needed for using a digital counter here. It is impossible to count directly the harmonic-rich signal from the instrument and thus get the fundamental frequency of the tone. Such a direct count gives randomly varying numbers much higher than the fundamental. One must add a low-pass filter set to remove most of the overtone content. For the trombone, cutoff frequencies of 150-300 Hz are appropriate. A tunable filter, such as the old Pasco Fourier analyzer, is most convenient for this application.

I feel this simple demonstration is rather effective, and it always delights the students to see the hose in the bell.

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25 June 1985

<sup>1</sup>B. W. Holmes, *Am. J. Phys.* **53**, 504 (1985).

### THE SURFACE OF WATER, OR ICE

In the first "Search for Simplicity," Weisskopf<sup>1</sup> attributed the fact that for water the molecular binding energy at

the surface is more than  $\frac{1}{2}$  of the one in the interior, to the shape of the water molecule. In his view, the superficial water molecules would lie with their dipoles parallel to the surface, so that less of the binding energy is lost (compared to the interior) than with molecules for which the binding is spherically symmetric.

However, the existence of a quadrupole moment<sup>2</sup> in water molecules implies an asymmetry in their dipoles; it could be energetically favorable for surface molecules to be oriented with their dipoles directed into,<sup>3</sup> or out of,<sup>4</sup> the surface. The existence of such a transition region on the water surface, particularly in the solid form, could be related<sup>5</sup> to the many peculiar properties of ice. A liquidlike, disordered region on the surface of a solid, while still below its melting point, may exist not only in ice but also in lead<sup>6</sup> and copper.<sup>7</sup>

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<sup>1</sup>V. Weisskopf, *Am. J. Phys.* **53**, 19 (1985).

<sup>2</sup>See, e. g., R. M. Glaeser and C. A. Coulson, *Trans. Faraday Soc.* **61**, 389 (1965).

<sup>3</sup>N. H. Fletcher, *Physics and Chemistry of Ice*, edited by E. Whalley, S. J. Jones, and J. W. Gold (R. Soc. Can., Ottawa, 1973), p. 132.

<sup>4</sup>G. J. Turner, *Philos. Mag. A* **48**, L45 (1983).

<sup>5</sup>G. J. Turner and C. D. Stow, *Philos. Mag. A* **49**, L25 (1984).

<sup>6</sup>J. Frenken and J. F. van der Veen, *Phys. Rev. Lett.* **54**, 134 (1985).

<sup>7</sup>C. S. Jayanthi, E. Tosatti, and L. Pietronero, *Phys. Rev. B* **31**, 3456 (1985).

## RESPONSE TO TURNER'S "THE SURFACE OF WATER, OR ICE"

Turner is an expert on the structure of water and is justified in criticizing my assumption that surface water molecules have their dipoles parallel to the surface. However, whatever the energetics of the interaction demand, they will arrange themselves such that the energy at the surface is lowered. This is all that is necessary to understand in a qualitative way that less of the binding is lost at the surface, than with molecules for which the binding is symmetric.

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## THE SI IS NOT IDEAL FOR TEACHING ELEMENTARY ELECTROMAGNETISM

Nearly 35 years ago the "Report of the Coulomb's Law Committee of the AAPT" was published in this journal.<sup>1</sup> It recommended the abandonment of the earlier approaches to electromagnetism based on the cgs system of units in favor of what today is called the SI approach, which combined the so called "practical units" such as ampere, volt, farad, etc. with the absolute mks units. For more than 100 years, teaching of electromagnetism was based on the esu, emu, and Gaussian systems, all derived from the proposals made first by Gauss and Weber, and then by Maxwell, Kelvin, Joule, and other great scientists.

Transition from the earlier systems to the SI was far from smooth; many scientists opposed it on various grounds, as vividly recorded by Varney.<sup>2</sup> But, finally, the new system prevailed and by now much experience has been accumulated in using it in elementary physics. Teaching experience shows that it is practically impossible to deal with  $\epsilon_0$  and  $\mu_0$  in a logically consistent manner. These artificial dimensional factors are always introduced in a postulatory way or supported by arguments such as "why not" and "it will be clear in the future." Like the so-called "new math," the SI approach is too formal and perhaps is partially responsible for the declining interest in physics among our youngsters.

The situation can be remedied without returning to the hodgepodge of approaches which existed prior to the introduction of the SI. It is possible to create a set of teaching units for electromagnetism based on the mechanical units of the SI and supplemented by a new unit of charge. Like the old stacoulomb, the new unit of charge would be defined by the Coulomb's law, but with  $F$  in newtons and  $r$  in meters. Other units would be developed progressively as in the old esu system, matching the order in which we teach the subject in the introductory courses. Instead of artificial  $\epsilon_0$  and  $\mu_0$ , only one natural factor, the speed of light, would appear in the equations dealing with electromagnetism.

It is true that this approach would generate units which are most often different from those of the SI, but per-

haps this price is worth paying for the benefit of clarity. Inconveniences associated with the symbiotic coexistence of two systems of units (not four as it used to be) would be much less damaging than circular reasoning built into the ways in which electromagnetic phenomena are now described and passed from one generation to another. An introductory course does not have to be a diluted version of an advanced description. We should build on what is below and not on what is above. Unfortunately, the SI approach to electromagnetism does not facilitate this natural methodology.

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<sup>1</sup>*Am. J. Phys.* **18**, 1 (1950).

<sup>2</sup>R. N. Varney, *Am. J. Phys.* **8**, 222 (1940).

## A SIMPLE FIRST-ORDER TEST OF SPECIAL RELATIVITY

There is a basic flaw in the analysis of the Fresnel drag in the paper by Byl *et al.*<sup>1</sup> The corresponding flaw in my own paper<sup>2</sup> which is quoted in Ref. 1, was the subject of comment by Zhang.<sup>3</sup>

Although Eq. (8) reduces to  $c' = c$  when  $n = 1$ , the speed  $c'$  is relative to the ether, whereas in the analysis in the paper it is assumed to be relative to the apparatus. As referenced on the ether, the lengths of the ray paths change during their transit. To assume that these paths are fixed in length the light speed in top beam is  $c - v$  and that in the lower beam is  $c/n + (1 - 1/n^2)v - v$  or  $c/n - v/n^2$ . To first order in  $v/c$  the transit times over the same length are proportional to the inverse of these, namely to  $1 + v/c$  and  $n(1 + v/cn)$ . The difference is independent of  $v/c$ , meaning that no first-order measurement of speed anisotropy is possible by the proposed method.

Even so, it should not be supposed that first-order measurements are not feasible. When waves are reflected back upon themselves, as in the Michelson-Morley experiment, standing waves are formed with electrical field nodes locked onto the mirror surface. We then have no certain knowledge



mountains formed by volcano activity. But there is no reason why such mountains would reach the maximum height.

Incidentally I would like to correct a misprint in that column. The melting heat  $\epsilon_M = 0.089$  and not 0.148 eV. However the estimate of the height of the mountain was made with the correct value. There is also some confusion in the notation in the first formula on p. 111, but the final values are correct.

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# NOTE ON "THE AXIOMS UNDERLYING MAXWELL'S ELECTROMAGNETIC EQUATIONS" [G. B. WALKER, AM. J. PHYS. 53, 1169 (1985)]

The passage of over 35 years since the appearance of our "Note on the Presentation of Maxwell's Equations" in this very Journal<sup>1</sup> makes it understandable that Professor G. B. Walker might have overlooked our work in preparing his insightful article. We had discussed how certain combinations of

$$\text{Gauss's law } \nabla \cdot \epsilon_0 \mathbf{E} = \rho, \quad (1)$$

$$\text{Ampere's law } \nabla \times \mathbf{H} = \mathbf{J}, \quad (2)$$

Conservation of charge

$$\nabla \cdot \mathbf{J} + \dot{\rho} = 0, \quad (3)$$

Maxwell's 2nd equation without charges

$$\nabla \times \mathbf{H} = \epsilon_0 \ddot{\mathbf{E}}, \quad (4)$$

Maxwell's 2nd equation with charges

$$\nabla \times \mathbf{H} = \epsilon_0 \ddot{\mathbf{E}} + \mathbf{J}, \quad (5)$$

imply the remaining equations. In particular we demonstrated how the combination (1), (3), and (4) leads to (5), and thence trivially to (2). We paid particular attention to accommodating the singularities engendered by the passage of point charges through surfaces of integration. Professor Walker does essentially the same thing, with perhaps less worry about the singularities. We share with Professor Walker the value of the insight afforded by seeing how displacement current implies the magnetic field associated with a current. In fact, we wrote

"...It appears to us that a more suitable method of correlating the concepts (of conduction current and dis-

placement current) is to begin with the displacement current as fundamental, and then proceed to interpret conduction current as a phenomenon of the same nature, magnetically, as the motion of the electric fields surrounding the moving charged particles that constitute the conduction current."

But as much as this view appeals to us, we are not so confident as to which laws should be considered "facts," "doctrines," "axioms," or whatever. That, however, is another story.

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<sup>1</sup>John P. Vinti and D. J. X. Montgomery, Am. J. Phys. 17, 298 (1949).

# REPLY TO THE NOTE BY VINTI AND MONTGOMERY

At first sight it may appear that the two papers cover the same ground and differ only in detail in the calculation of the magnetic effect of a current of point charges. In fact, the subject of Maxwell's equations is approached in very different ways.

The objective of the Walker paper is to examine the following question. Assuming Maxwell's equations to be correct in a particular inertial reference frame (as defined by Einstein) what in fact are the laws of nature underlying these equations? The objective of the paper by Vinti and Montgomery, as stated on p. 299, is to show how one of Maxwell's equations can be derived from a form of that equation (omitting the term indicating electric current density) by the explicit use of an equation expressing conservation of charge. In other words, they are concerned primarily with a mathematical issue and in their current note quite properly refer to the Walker paper as "another story."

It is to be hoped that the two papers will stimulate interest in basic questions in electromagnetism which for many years have come to be regarded as dead issues by teachers, writers, and journal review boards. That flaws in

Maxwell's arguments have been exposed is surely reason for teachers to be wary of repeating these same arguments solely on the grounds of tradition. My only criticism of the excellent paper by Vinti and Montgomery is that they continue to speak of "displacement current" a phrase Maxwell himself might now regret having introduced.

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# ON MAXWELL'S FAITH

Paul Theerman's recent article<sup>1</sup> neglected two interesting points regarding James Clerk Maxwell's faith. As Korg<sup>2</sup> has pointed out, the Victorians, among their many phobias, had a tendency to express a kind of "theological agoraphobia," if you will, after learning that the Earth was a minute speck lost in the immensity of the universe. Tennyson, who wrote *In Memoriam*, *AH*—the credo which sums up the nineteenth century crisis of faith—called these vast reaches "the waste places of the sky" (Canto 3). Perhaps Maxwell envisioned future generations cured of this despair by the good news to be discovered in his electromagnetic theory. Because the luminiferous aether "fills the smallest portion" of this immensity, Maxwell believed he had not only unified electricity and magnetism, but had bound the great universe together in unity, as well. Here he seems to be addressing Tennyson.

The vast interplanetary and interstellar reaches will no longer be regarded as waste places in the universe, which the Creator had not seen fit to fill with the symbols of the manifold order of his kingdom.<sup>3</sup>

As for F. D. Maurice, Theerman did not describe the radical implications of his theology, which had him briskly trounced from King's College. In brief, Maurice seemed to interpret the famous phrase, "The kingdom of God is at hand," to mean, "The kingdom of God is at hand, at your very fingertips—in this life, not necessarily in some afterlife. Pick it up and grasp onto it." For his damage to the promise of afterlife, Maurice was regarded as dangerous; as poison.

The interesting question that remains is not so much why Maxwell embraced this enlightened view and

## Search for Simplicity: Quantum mechanics and the Pauli principle

Victor F. Weisskopf

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## ADVERTISEMENT





## Search for Simplicity: Quantum mechanics and the Pauli principle

Quantum mechanics is based upon the wave-particle duality. An entity such as an electron exhibits both wave and particle properties. It is neither a particle or a wave in the classical sense. Let us call it a "wavicle," an expression introduced by Eddington in his 1927 Clifford Lectures. The physical state of a wavicle or of a group or wavicles, "the quantum state," is described by a wave function, a mathematical expression from which the results of any experimental observation can be deduced according to well-established rules. In these essays, we will rarely enter into a detailed discussion of wave functions.

The connection between the wave and particle aspects are established by the DeBroglie relations. The momentum  $p$  and energy  $E$  of the particle, the wavenumber  $k$ , and frequency  $\omega$  of the wave, are related to each other, when "particle" and "wave" are the two aspects of the same wavicle. (The wavenumber  $k$  is defined by  $k = \lambda^{-1}$ ,  $\lambda = \lambda/2\pi$ , where  $\lambda$  is the wavelength; the frequency  $\omega$  is  $2\pi$  times the number of up and downs per second.) These relations are

$$p = \hbar k, \quad E = \hbar \omega, \quad (1)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$  ( $\hbar \sim 10^{-27}$  erg s).

Two conclusions emerge from this. It is known that waves confined to a finite volume must be superpositions of vibrations of a series of definite frequencies  $\omega_i$ . Therefore an electron, when confined in space, can only assume certain energy values  $\hbar\omega_i$  which we call the *spectrum*. Furthermore, the wave vibrations corresponding to these values have well-defined shapes. In ordinary matter this confinement is due to the electrostatic attraction by the nuclei within atoms. Thus specific shapes and forms enter into physics as a necessary step. This is one of the important insights of quantum mechanics into the origin of well-defined shapes which abound in nature. That "morphing" trait is the ultimate cause that the same flowers appear each spring, whose properties are governed by the electron configurations in the DNA molecules.

The second conclusion has to do with the lowest kinetic energy of a single wavicle confined to a restricted region in space. Necessarily the lowest wave shape will be a superposition of plane waves with  $\lambda$  of the order of the linear dimensions  $R$  of the confinement. Since the kinetic energy  $K$  is  $p^2/2m$ , where  $m$  is the mass of the wavicle (we are dealing with nonrelativistic cases), the minimum value is of the order

$$K_{\min} \sim \hbar^2/(2mR^2). \quad (2)$$

What is the minimum kinetic energy if more than one particle are confined to a volume  $V \sim R^3$ ? If the particles are equal (including spin) we must make use of the Pauli principle. We formulate the principle for our purposes in the following way: If  $N$  equal particles are confined in a volume  $V \sim R^3$ , they cannot be all in the lowest state with  $\lambda \sim R$ . One obtains the average kinetic energy by assuming that each of the  $N$  particles is confined to a volume  $V/N$ . The Pauli principle acts as if each particle has its "private room."

Therefore the minimum total kinetic energy of  $N$  equal particles in a volume  $V$  is

$$K_{\min} = \kappa N \hbar^2 / 2m d^2, \quad d^3 = V/N, \quad (3)$$

where  $\kappa$  is a constant of order unity. When we are dealing

with electrons in a volume  $V$ , two electrons with opposite spin can be in one "private room." This does not change the order of magnitude of the kinetic energy (3). For this case a more quantitative calculation gives the value

$$\kappa = (3/5)(3\pi^2)^{2/3} = 5.7 \quad (4)$$

for simple volumes such as a cube or a sphere.

The kinetic energy (3) increases with decreasing confining volume. It takes work to compress wavicles. We therefore speak of a "Schrödinger pressure"  $P$  which a wavicle or  $N$  wavicles in their lowest states exert towards the outside, in contrast to classical physics where all particles are at rest in the lowest state and do not exert any pressure.  $P$  is the (negative) derivative of the minimum kinetic energy:

$$P = - \frac{dK_{\min}}{dV} = \kappa' \frac{\hbar^2}{2m} \left( \frac{N}{V} \right)^{5/3}. \quad (5)$$

In the case of electrons confined to a volume  $V$ ,  $\kappa' = (2/5)(3\pi^2)^{2/3} = 3.8$ . Consider, for example, the conduction electrons of a metal. In simple metals, such as the alkali metals, there is one electron per atom moving more or less freely within the metal, forming an "electron gas." Inserting a plausible value  $d = (N/V)^{1/3}$  of  $2.5 \times 10^{-8}$  cm into (5) we get a Schrödinger pressure of a quarter of a million atmospheres. The metal does not explode because the electrons are contained by the electrostatic attraction of the ions. When a metal is compressed the kinetic energy goes up as  $d^{-2}$ , whereas the Coulomb attraction rises only as  $d^{-1}$ , or even less since the Pauli principle does not allow the conduction electrons to penetrate into the electron shells of the ions. Therefore compression is resisted by a good fraction of the Schrödinger pressure. Indeed, pressures of that order are necessary to reduce the volume of a metal by a significant amount (say 20%).

The resistance against pressure is measured by the bulk modulus  $B$ . It has the dimension of a pressure. If  $n\%$  of the pressure  $B$  is applied, the volume decreases by  $n\%$ . Table I shows  $P$  in ergs/cm<sup>3</sup> calculated by means of (5) compared with the observed bulk modulus<sup>1</sup> for alkali metals. One atmosphere is  $10^6$  ergs/cm<sup>3</sup>.

Indeed,  $P$  is of the same order of magnitude as  $B$  but somewhat smaller with the exception of Li. The additional effect comes from the electron clouds around the ions which can be considered as an electron gas confined to the ionic volume. They also resist compression. The higher  $Z$ , the larger are the ions and the more important is their role. We only considered the effect of the almost free conduction electrons because it is simple to calculate their Schrödinger pressure.

The resistance to compression of nonmetallic materials is solely caused by the electron clouds around the atoms. It is not easy to find an approximate expression for this effect.

Table I.  $P$  in ergs/cm<sup>3</sup> compared with the observed bulk modulus for alkali metals.

Metal	Li	Na	K	Rb	Cs
$d \times 10^8$ cm	2.8	3.4	4.2	4.4	4.8
$P \times 10^{-11}$	1.4	0.51	0.18	0.14	0.09
$B \times 10^{-11}$	1.2	0.68	0.32	0.31	0.20

What counts are the outer electrons, since the inner ones are held tightly by the nuclei. Thus the expected pressure resisting compression should correspond very roughly to an electron gas with several electrons per atom. We therefore expect values of the same order but somewhat larger than the ones for a gas of one free electron per atom. Whenever you feel in your daily life the hardness of solids, be they metals, rocks, ceramics, or wood, remember that it is the Schrödinger pressure which causes it, the resistance of electrons being forced to assume smaller wavelengths.

Here is a question which will be answered in the next installment: How can we understand the “private room” concept as a consequence of the Pauli principle?

Answer to the question of the first installment: Let us cut

into a cubic centimeter of a solid which we assume to be a crystal. Let the cut be along a crystal plane. We certainly need a strong force, but the two halves fall apart by themselves when the cleaving has created a split of the order of a lattice distance  $d$ . That needs only a penetration of a few  $d$ . Thus the *energy* (force times distance) of producing two surfaces is about as small as in a liquid. The cutting of a liquid sample requires a weak force but it is applied all the way through.

Victor F. Weisskopf

<sup>1</sup>C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), 5th ed., p. 85.

## Search for Simplicity: Quantum mechanics of atoms

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: Quantum mechanics of the hydrogen atom

In the last essay we introduced the minimum kinetic energy  $K_{\min} \sim \hbar^2/(2mR^2)$  of an electron of mass  $m$  confined to a volume of linear dimension  $R$ . We observed that it will try to expand (Schrödinger pressure) if it is not kept from doing so by a confining force. With these concepts we can directly determine the energy and size of the hydrogen atom. The electron wavecloud surrounds the nucleus in a spherical cloud with an average radius  $R$ . The lowest state is the result of two forces in equilibrium: the electrostatic attraction  $e^2/R^2$  of the nucleus and the tendency of the cloud to expand. This tendency can also be expressed in terms of a force, the "Schrödinger force." Whenever an energy depends on a coordinate  $x$ , there is a force to change  $x$ ; it is the negative derivative of the energy with respect to  $x$ . Thus the Schrödinger force is the negative derivative of the minimum kinetic energy with respect to  $R$ . Setting these two opposing forces equal gives

$$\frac{e^2}{R^2} = -\frac{dK_{\min}}{dR} \sim \frac{\hbar^2}{mR^3}. \quad (1)$$

That relation determines  $R$ , which happens to come out equal to the "Bohr radius":

$$R \sim \hbar^2/(me^2) \equiv a_B = 0.53 \times 10^{-8} \text{ cm}. \quad (2)$$

The energy  $E$  of the electron in this state is

$$E \sim -\frac{e^2}{R} + \frac{\hbar^2}{2mR^2}. \quad (3)$$

Inserting (2) gives

$$E \sim -me^4/2\hbar^2 = -\frac{1}{2}e^2/a_B = -13.6 \text{ eV}. \quad (4)$$

The energy  $|E|$  is called Ry(rydberg); it is the amount necessary to liberate the electron. It is remarkable that we get the exact result for the ionization energy of hydrogen by using our approximate estimates.

The relation (1) happens to be the condition for the energy (3) to be a minimum. Therefore the results (2) and (4) can also be interpreted as resulting from finding the lowest possible value of the energy as one would expect for the lowest quantum state.

The excited states of hydrogen can be found by a similar procedure. Higher quantum states have  $n$  nodes in their wave functions. Then the characteristic wavelength  $\lambda$  is  $R/n$ , giving rise to a higher kinetic energy  $K_n \sim n^2\hbar^2/(2mR^2)$ . The corresponding stronger expanding force

$$-\frac{dK_n}{dR} = \frac{n^2\hbar^2}{mR^3}$$

is balanced by the Coulomb attraction  $e^2/R^2$  and gives rise to larger radii  $R_n = n^2\hbar^2/(me^2)$ . Inserting this into the energies  $E_n = -e^2/R + K_n$  yields the well-known Balmer formula  $E_n = -(me^4/2\hbar^2)(1/n^2)$ . Note that the energy is smaller than  $mc^2$  by a factor  $(e^2/\hbar c)^2$  which shows that the use of a nonrelativistic expression for kinetic energy is justified.

What about atoms with more than one electron? We will treat helium and atoms with many electrons in greater detail later on. For the moment we use a very crude picture: such atoms contain a core consisting of the nucleus and most of the electrons. It carries a charge  $ne$  where  $n$  is the small number of the remaining outer electrons. Thus, qualitatively, the situation is not unlike an atom with a few electrons. We then expect again dimensions of the order  $a_B$

and an energy of the order of a Ry to liberate one of these outer electrons.

These results are perhaps the greatest triumph of quantum mechanics. The existence of atoms was known for a century and conjectured for many more, but their size and internal energies were only deduced from experiments such as the ones mentioned in the previous essay. Quantum mechanics showed that they are of the order of  $a_B$  and of Ry, respectively, both of which are simple combinations of the three fundamental constants,  $m$ ,  $e$ , and  $\hbar$ .

It is instructive to apply the same method to nuclear systems. The force between the nucleons is more complicated than the Coulomb force; it is repulsive for small distances and drops exponentially for larger ones. We may very roughly approximate the potential of the attractive part by  $-g^2/r$ . Figure 1 shows that  $g^2 \sim 10e^2$  (taken from Ref. 1). It is about ten times stronger than the attraction between two opposite charges  $e$ . The repulsion at the center is important—it keeps the nucleons apart—but does not influence the energy very much because it acts only at distances which will turn out to be much smaller than the separations between nucleons. Replacing the electron mass by the nucleon mass  $M \sim 2000m$  and  $e^2$  by  $g^2$ , we obtain for the nuclear Bohr radius  $a_N$  and the nuclear rydberg  $Ry_N$

$$a_N \sim a_B/20\,000 = 2.7 \times 10^{-13} \text{ cm},$$

$$Ry_N \sim 200\,000 \text{ Ry} = 2.7 \text{ MeV}.$$

These are indeed typical distances and energies in nuclear physics, but they are very rough estimates, not only because of the complicated form and of the symmetry dependence of the nuclear force but also because of the intricacies of the many-body problem in ordinary nuclei. For the deuteron, however, our method should give reasonably good results if we replace  $M$  by the effective mass  $M/2$ . This would double  $a_N$  and halve  $Ry_N$ , not too far from the actual values  $4.3 \times 10^{-13} \text{ cm}$  and  $2.2 \text{ MeV}$ .

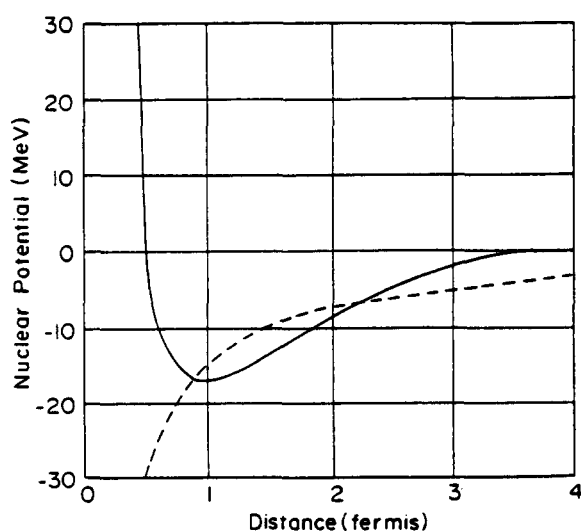


Fig. 1. Sketch of the potential of the nuclear force as a function of internucleon separation as measured in fermis,  $10^{-13} \text{ cm}$ . (This curve is not quantitative, because it ignores the dependence on spin and symmetry.) For comparison, the dashed curve gives the attraction of two opposite, but equal, charges  $3.2e$ . [Reprinted from Ref. 1.]

We now answer the question of last month as to why the Pauli principle is equivalent to the assumption that each of  $N$  equal particles in a volume  $V$  is confined to a "private" volume  $V/N$ . There are two explanations. Here is the first. A quantum state of a free particle with a well-defined momentum is stationary; its momentum stays constant and its position is spread over the whole volume  $V$ . This is not the only kind of state. We can construct nonstationary states where the momentum and the position are spread over finite intervals  $\Delta x$  and  $\Delta p$  which obey Heisenberg's relation  $\Delta x \Delta p = \hbar$ .  $N$  equal particles must be distributed over  $N$  different quantum states. Let us choose states that are blobs of a spatial extension  $\Delta x$  and which have all the same momentum distribution. To prevent any overlap the size  $\Delta x$  must be smaller or equal to  $d = (V/N)^{1/3}$ . We choose the maximum  $\Delta x \sim d$  in order to minimize the momentum spread  $\Delta p$ . This leads us directly to the "private room" of dimension  $d$ , and to an average momentum  $\sim \hbar/d$ .

For the second approach we remember that the Pauli principle is equivalent to the antisymmetry of the wave function  $\Psi$ . The latter changes sign if the coordinates of two equal particles are exchanged. From this follows immediately that the wave function vanishes if two equal particles have the same coordinates; they cannot be at the same

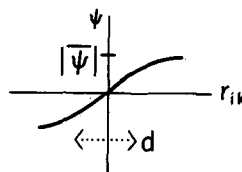


Fig. 2. Dependence of the wave function on the relative distance of two equal particles.

place. (This is the last remnant of the classical concept of impenetrable particles.) Let us look at the dependence of  $\psi$  on the distance  $r$  of two electrons (Fig. 2). It is zero for  $r = 0$  and reaches its typical values  $\pm |\bar{\psi}|$  roughly like  $\psi \sim \bar{\psi} \sin kr$  between  $r = -\pi/2k$  and  $+\pi/2k$ . This is a wave function corresponding to a relative momentum  $p_r = \hbar k$ . The probability  $|\psi|^2$  is low as long as  $|r| < k^{-1}$ . Thus the electrons stay apart at a distance of the order of  $d \sim \hbar/p_r$ . The average momentum  $p$  of the electrons is of the same order as the relative momentum  $p_r$ , and we get again the relation  $p = \hbar/d$  between the momentum and the size  $d$  of the "private room."

Victor F. Weisskopf

<sup>1</sup>K. Gottfried and V. Weisskopf, *Concepts of Particle Physics* (Oxford University Press, New York, 1984).

## Search for Simplicity: Atoms with several electrons

Victor F. Weisskopf

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## ADVERTISEMENT





## Search for Simplicity: Atoms with several electrons

We can use the methods applied to the hydrogen atom in the previous essay for the study of atoms with several electrons. Let us first look at helium. Here we have two electrons with opposite spin in the ground state, considered as a cloud with some kind of average radius  $R$ . The energy  $E$  is then

$$E \sim -\frac{4e^2}{R} + \frac{e^2}{r_{12}} + 2\frac{\hbar^2}{2mR^2}. \quad (1)$$

The first term is the potential energy of the two electrons in the field of the doubly charged nucleus. The second term is the repulsion between the electrons; the third term represents the kinetic energies of both electrons. Since  $R$  and  $r_{12}$  appear always in the denominator, we define  $R^{-1}$  as the average of the reciprocal distance of the electrons from the center and  $r_{12}^{-1}$  as the average of the reciprocal distance between them. We put  $r_{12} = R/\beta$  and expect  $\beta$  to be less than unity since  $r_{12}$  will be larger than the average distance  $R$  from the center. We write the energy (1) in the form

$$E = -\frac{A}{R} + \frac{B}{2R^2}, \quad A = (4 - \beta)e^2, \quad B = 2\hbar^2/m. \quad (2)$$

Let us remember once for all—we will need it in later essays also—that the minimum of  $E$  and the corresponding  $R$  are given by

$$E = -A^2/2B, \quad R = B/A. \quad (3)$$

We find for helium

$$E = -(4 - \beta)^2 \frac{e^4 m}{4\hbar^2}, \quad R = \frac{2}{(4 - \beta)} \frac{\hbar^2}{me^2}. \quad (4)$$

How do we find the values of  $\beta = R/r_{12}$ ? Both  $R$  and  $r_{12}$  depend on the shape of the electron distribution  $\rho(r)$ , the density of electrons at the distance  $r$  from the center. The radius  $R$  is defined by  $R^{-1} = \int (\rho/r) dx^3$ , where  $\int dx^3$  is an integration over all space.  $r_{12}$  can be found by calculating the electrostatic energy  $\epsilon$  of two identical electron clouds  $\rho(r)$ :  $\epsilon = e^2/r_{12}$ . This calculation is simple but lengthy. The best way to do it is to calculate the electrostatic potential  $U(r)$  produced by the charge distribution  $e\rho(r)$ . Then,

$$\epsilon = e \int dx^3 U(r) \rho(r) = \frac{e^2}{r_{12}}$$

which determines  $r_{12}$ . A rectangular charge distribution gives  $\beta = 0.8$ ; an exponential dependence ( $\rho \sim e^{-r/b}$ ) leads to  $\beta = 5/8$ . The more  $\rho$  increases towards the center, the lower is  $\beta$ . Here is something to think about: why is  $\beta$  smaller for distributions packed towards the center? (The answer will appear in the next issue.)

Let us return to helium. The simplest assumption would be a rectangular distribution with  $\beta = 0.8$ , which gives  $E = 5.1$  Ry according to (4). We may use our knowledge that the distribution drops off exponentially with  $\beta = 5/8$ . Then we get

$$E = -5.7 \text{ Ry}, \quad R = 0.59a_B, \quad \text{Ry} = me^4/2\hbar^2, \quad (5)$$

where  $a_B$  ( $a_B = \hbar^2/me^2$ ) is the Bohr radius. The actual energy to remove the two electrons is 5.81 Ry. Again, it is remarkable how close these crude considerations come to the correct results.

We can apply similar methods to the determination of ionization energies and electron affinities of atoms of 3 to 10 electrons. This was done in a paper by M. Kregar and the author which was published in this journal,<sup>1</sup> so that we do not need to repeat it here.

We now turn to atoms with many electrons. We generalize expression (1) to  $Z$  electrons around a fixed point charge  $Ze$  and assume  $Z \gg 1$ . This will get us what I like to call “the poor man’s Thomas–Fermi method.” We get, instead of (1),

$$E = -\frac{Z^2 e^2}{R} + \frac{Z(Z-1)}{2} \frac{e^2 \beta}{R} + Z \frac{\hbar^2}{2mR^2} \left(\frac{Z}{2}\right)^{2/3}. \quad (6)$$

The first term is the potential energy of  $Z$  electrons attracted by the nucleus, and  $R$  is an average distance from the center. The second term comes from the repulsion between the electrons. There are  $Z(Z-1)/2$  pairs, each giving rise to a potential energy  $e^2/r_{12}$ , where  $r_{12} = R/\beta$  is an average of the distance between electrons, as we had it in helium. The difference with helium shows up in the kinetic energy. The Pauli principle must be considered when there are more than two electrons. Each electron shares a “private room” of a linear dimension  $\tilde{r}$  with a partner of opposite spin. There must be  $Z/2$  such rooms within the electron cloud of dimension  $R$ , so that  $(Z/2)\tilde{r}^3 = R^3$ . The minimum kinetic energy per electron is  $\sim \hbar^2/(2m\tilde{r}^2)$  which explains the third term in (6).

We may replace  $Z(Z-1)$  by  $Z^2$  and get

$$E = -\frac{A}{R} + \frac{R}{2R^2}, \quad A = Z^2 e^2 \left(1 - \frac{\beta}{2}\right),$$

$$B = Z^{5/3} \frac{\hbar^2}{2^{2/3}m}.$$

According to (3), this is a minimum when

$$R = \frac{a_B}{(1 - \beta/2)2^{2/3}Z^{1/3}},$$

$$\frac{E}{Z} = -2^{2/3}Z^{4/3} \left(1 - \frac{\beta}{2}\right)^2 \text{ Ry}. \quad (7)$$

We will show below that  $\beta = 0.36$ , which is much smaller than in helium. This is because the charge distribution is strongly pointed toward the center. With that value we find

$$R = 0.77Z^{-1/3}a_B,$$

$$-\frac{E}{Z} = 1.06Z^{4/3} \text{ Ry} = 14.4Z^{4/3} \text{ eV}. \quad (8)$$

This is the average binding energy of an electron. The actual value is  $16Z^{4/3}$  eV. The usual Thomas–Fermi method gives  $20Z^{4/3}$  eV. Poor man is better than affluent man!

We need the electron distribution  $\rho(r)$  in order to determine  $\beta$ . We choose a simple and plausible distribution:

$$\rho = Ae^{-(r/b)}/r^n. \quad (9)$$

Electron densities are expected to exhibit an exponential decrease, albeit not as simply as in (9). The factor  $r^{-n}$  is included in order to assure that  $\rho$  has the correct behavior near the center: There should be about two electrons within the radius  $r_K = a_B/Z$  of the  $K$ -shell, a number which is independent of  $Z$ . (The  $S$ -states of outer shells contribute a negligible amount.) The three constants  $A$ ,  $b$ ,  $n$  in (9) are

determined by the following conditions imposed on  $\rho$ :

$$\begin{aligned} 4\pi \int_0^\infty \rho r^2 dr &= Z, & 4\pi \int_0^{a_B/Z} \rho r^2 dr &= "2", \\ 4\pi \int_0^\infty \rho r dr &= \frac{Z}{R}. \end{aligned} \quad (10)$$

The first condition assures that there are  $Z$  electrons; the second determines the number of electrons with the  $K$ -shell. The symbol "2" is used because we only need this number to be independent of  $Z$  and near 2. The third condition assures the average of  $r^{-1}$  for each electron is  $R^{-1}$  as used in (6).

We do not show the details of the simple integrations (10). One determines  $A$  from the first integral; the condition that the second should be independent of  $Z$  determines  $n$ ; the third integral is used to express  $b$  in terms of  $R$ . The results of (10) turn out to be

$$4\pi A = 2Z/(\pi^{1/2} b^{3/2}), \quad n = 3/2, \quad b = 2R. \quad (11)$$

We obtain  $\beta$  for the distribution (9) with the constants (11) by using the methods mentioned before. The calculations are even lengthier than those for the simpler distributions which we considered for helium, but there is no fundamental difficulty. The result turns out to be  $\beta = 1 - 2/\pi = 0.36$ , the value which we used in (7) to determine the energy of the atom and the length  $R$ .

We can use the electron distribution (9) to get an idea of the atomic size. The magnitude  $R$  is not the radius  $R_a$  of the atom; it is the average distance of the electrons from the center and, therefore, much smaller than  $R_a$  since most of the electrons are in the inner parts. In order to get an estimate of the size of the atom, we must find out the extension of the distribution (9). Literally, it goes to infinity, but we may get a rough value of the atomic radius  $R_a$  by finding the radius at which, say, one half of the last electron is left outside. This distance indicates where the last electron may be found. In other words,  $R_a$  is given by the integral

$$4\pi \int_{R_a}^\infty \rho r^2 dr = \frac{1}{2}. \quad (12)$$

Table I. Estimates of atomic radii.

$Z$	$y$	$R_a/a_B$
30	10.04	2.49
50	11.16	2.33
90	12.42	2.13

The evaluation of this integral leads to the following equation for  $y = R_a/R$ :

$$2\pi/(4Z)^2 = ye^{-y}.$$

We then obtain, for three values of  $Z$ , the radii found in Table I. The atomic radius turns out to be almost independent of  $Z$ . The decrease of  $R$  as  $Z^{-1/3}$  is compensated for by the fact that the exponentially decaying  $\rho$  must reach farther out to get to the last electron. One should conclude from this result only that atomic radii do not depend much on  $Z$  and are of the order of a few Bohr radii. The slight decrease of  $R_a$  in Table I is not a real effect; it comes from the simple exponential form (9) of the electron distribution. Actually, the exponential decrease is much sharper near the center than farther away, because the effective charge of the core is higher for the inner electrons. This effect is more pronounced for higher  $Z$  and has a strong influence on the determination of  $R_a$  by the integral (12). It would increase the radii.

The homework to this essay, of course, is to perform the indicated calculations of the constants (11), of the  $\beta$  values for the different distributions, and of  $R_a$ .

Victor F. Weisskopf

<sup>1</sup>M. Kregar and V. F. Weisskopf, *Am. J. Phys.* **50**, 213 (1982).

*Addendum:* The ideas presented in the January essay have been published as early as 1858 by J. J. Waterton [*Philos. Mag.* **15**, 1 (1858)] as pointed out by A. P. French [*Am. J. Phys.* **35**, 162 (1967)].

## PROBLEM

A cylindrical solid of any convex shape is rolling *under gravity* on horizontal plane. The potential energy  $V(s)$  can be represented<sup>1</sup> by  $V(s) = mg[\mathbf{r}(0)\mathbf{n}(0) - \mathbf{r}(s)\mathbf{n}(s)]$ , where  $\mathbf{r}(s)$  is the radius vector connecting the center of mass  $G$  of the rolling solid of mass  $m$  to the contact point  $M$ ,  $\mathbf{n}(s)$  is the inner normal,  $s$  is the curvilinear coordinate ( $s = 0$  corre-

sponds to the equilibrium at a point  $M_0$ ), and  $g$  is the gravity constant.

Find all curves  $\mathbf{r}(s)$  such that  $V(s)$  is identically zero [such that  $-\mathbf{r}(s)\mathbf{n}(s) = -\mathbf{r}(0)\mathbf{n}(0) = +h = \|G\mathbf{M}_0\|$ ]. (Solution is on page 349.)

<sup>1</sup>A. Ronveaux, *Am. J. Phys.* **52**, 618 (1984).

## Search for Simplicity: The molecular bond

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: The molecular bond

The chemical bond, the force that binds atoms to molecules, has curious properties. It is a force that acts only over short distances—a few atomic radii—it is attractive but becomes repulsive at smaller distances. Furthermore, attraction occurs only between certain combinations of atoms. The study of these rules is the subject of chemistry. Before quantum mechanics, chemistry and physics were different endeavors. Quantum mechanics can explain the properties of the chemical bond. Thus physics and chemistry became one science.

We start with the hydrogen molecule  $H_2$  from which we learn the nature of the “electron-pair” bond, the most important type. Consider two hydrogen atoms. We measure their distance by the distance  $\rho$  between the two nuclei. When  $\rho$  is much larger than the Bohr radius  $a_B = \hbar/me^2$ , there will be no force between them since they are electrically neutral. The energy  $E$  of the system will be simply the sum of the energies of the two isolated atoms:  $E = -2 \text{ Ry}$  for  $\rho \gg a_B$ , where  $\text{Ry} = -me^4/2\hbar^2$  (see the March essay). The vanishing of interaction at large  $\rho$  can be viewed as a cancellation of repulsive and attractive interactions: repulsions between the nuclei and between the electrons; attractions between each nucleus and the other atom's electron. (The attraction between the nuclei and their own electrons does not depend on  $\rho$  and is contained in  $E = -2 \text{ Ry}$ .)

What happens if  $\rho$  is no longer large compared to  $a_B$ ? Let us concentrate upon the part  $E'$  of the energy, which excludes the trivial repulsion energy  $e^2/\rho$  between the nuclei:  $E' = E - e^2/\rho$ . We know the values of  $E'$  for large  $\rho$ :

$$E' = -2 \text{ Ry} - e^2/\rho, \quad \rho \gg a_B. \quad (1)$$

But we also know  $E'$  for  $\rho = 0$ : It is the energy of two electrons attracted by a central charge  $2e$ . This is nothing else but helium! We determined that energy in the previous essay:  $E' = -5.7 \text{ Ry}$ . What happens to the repulsion of the two protons in helium? This question will be answered in the next installment.

We now make a rough approximation: We assume that (1) is valid for  $\rho > 2a_B$ . We interpolate  $E'$  between  $\rho = 0$  and  $\rho = 2a_B$  by a straight line (see Fig. 1). The actual energy  $E$  of the two hydrogen atoms is arrived at by adding  $e^2/\rho$  to  $E'$ . Obviously, this energy is  $-2 \text{ Ry}$  for  $\rho > 2a_B$ , and it has a minimum at  $\rho = \rho_0 = 1.22a_B$  as seen in Fig. 1. The minimum value is  $E(\rho_0) = -2.42 \text{ Ry}$ . For smaller  $\rho$ ,  $E$  rises strongly because of the preponderance of the repulsion between the nuclei.  $E(\rho)$  gives a good account of the chemical bond, its short range attraction and its repulsion at small distances. The position and depth of its minimum compares favorably with the actual distance  $1.43a_B$  of the nuclei in the hydrogen molecule and the actual binding energy of the H atoms, of  $0.34 \text{ Ry}$ . [The binding energy is the difference between  $E(\rho_0)$  and  $E(\infty)$  which is  $0.42 \text{ Ry}$  in our model.]

Figure 1 also shows  $E'(\rho)$  and  $E(\rho)$  as calculated exactly from the Schrödinger equation of two electrons in the field of two fixed unit charges at a distance  $\rho$ . We see that our bold linear approximation between  $\rho = 2a_B$  and  $\rho = 0$  for  $E'$  is not so bad. Compared to a smooth interpolation, it is a little too low for  $\rho \sim \rho_0$ ; this is why we get too deep a minimum and too large a binding. Furthermore the corner at  $\rho = 2a_B$  raises the energy around that distance and causes a steeper minimum and a smaller  $\rho_0$  than with the exact curve. Note that the true  $E'(\rho)$  has a horizontal tangent at

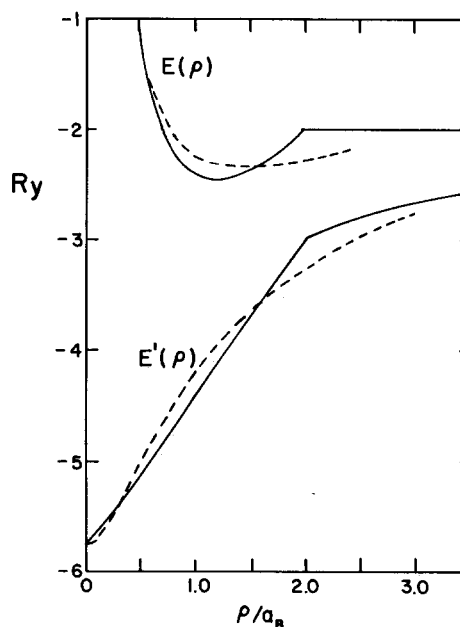


Fig. 1. Energy  $E$  of two hydrogen atoms as a function of the distance  $\rho$  between the nuclei.  $E'(\rho) = E - e^2/\rho$ . The energies are measured in Ry, the distance in units of  $a_B$ . The full curves are the approximate results, and the broken curves are the exact results.

$\rho = 0$  as expected since, at distances small compared to the Bohr radius for  $Z = 2$ , ( $a_B/2$ ),  $E'$  cannot differ much from the  $\rho = 0$  value.

Our conclusions are valid only if the two electrons have opposite spin. Only then does  $E'(\rho)$  go to the helium ground state for  $\rho = 0$ . If the spins are parallel, the lowest state in helium would be the triplet  $S$  state with an energy of  $-1.13 \text{ Ry}$ . Putting  $E'(0)$  equal to that value would lead to a curve of  $E'(\rho)$  which bends upwards going from  $\rho = 2a_B$  to zero. It would not give rise to values of  $E$  less than  $-2 \text{ Ry}$ ; there is no binding for parallel spins.

What is the physics that causes the minimum of  $E(\rho)$ ? When  $\rho$  becomes smaller than  $2a_B$  the electron clouds merge and the situation becomes similar to helium: either electron is attracted by the charge of both nuclei. This is counteracted by the increase in repulsion between the nuclei. The repulsion between the electrons is already considered in the value of the helium energy, where it plays an important role (see the April essay). But the double attraction wins out for values of  $\rho$  of the order of one-and-a-half  $a_B$ . The merging of the electron clouds is possible only if the electrons have different spin states. The Pauli principle would prevent the merging for parallel spin and would raise the energy because of the compression of the clouds when  $\rho < 2a_B$ .

These considerations show that the chemical bond is an electrostatic effect: The two electrons are exposed to twice as much positive charge within their clouds than in the separated atoms. This increased attraction is larger than the repulsions between the nuclei and between the electrons.

The chemical bond is often described as an “exchange effect.” I believe that such a formulation is misleading. It refers to mathematical terms appearing in the detailed calculation, in which two wave functions appear, differing by an exchange of coordinates. These terms are a consequence

of the Pauli principle requiring antisymmetric wave functions. They have no direct physical significance. Electrons are "exchanged" only in the sense that in the merged molecular quantum state it is no longer possible to assign an electron to one or the other nucleus.

The question left upon in the last essay was this. Why is  $\beta = R / r_{12}$  smaller for more peaked electron distributions  $\rho(r)$ ? Here  $R$  is an average of the distance from the center and  $r_{12}$  an average of the distance between two electrons distributed as  $\rho(r)$ . Take a given distribution  $\rho(r)$  and change it by moving a small part from a distance  $x$  to the center,

which would increase the peak. The contribution of this part to  $R$  goes from  $x$  to zero. However, the contribution to  $r_{12}$  goes from a certain value to another value larger than zero. Hence  $\beta$  would become smaller.

I use this occasion to thank Professor Herbert Bernstein of Hampshire College for most valuable discussions, and help in improving the clarity of presentation in this series.

Victor F. Weisskopf

## Response

Victor F. Weisskopf

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On chemical bonding

*Am. J. Phys.* **54**, 587 (1986)

On the kinetic energy of the electrons in metal formation

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## ADVERTISEMENT





$= 0.446$  Ry. Similarly, in the atomic state  $\bar{K}_{\text{at}} = I = 0.378$  Ry, thus the kinetic energy has increased by 0.068 Ry.

(2)  $E(r_s)$  is the energy of a "pseudo" electronic state, for which the increased attraction near the nuclei and the dynamical consequences of the Pauli principle are taken into account and simulated by a simple, smooth non-Coulombic pseudopotential, as explained in the essay. The energy  $E$  is the same for the actual and for the pseudo states, but not the kinetic and potential energies separately. In fact, the inverse cubic term in Eq. (3), though "potential energy" of the pseudostate, contains the increased kinetic energy of the actual state in the core region. Since the pseudopotential is not Coulombic, the pseudo kinetic and potential energies do not satisfy (i) and (ii) and that is why the pseudo  $\bar{K}$  may stay constant or even decrease on going from the atom to the metal.

In conclusion, bonding increases the electron kinetic energy. In the essay<sup>1</sup> the term "kinetic energy" is used in the sense of "kinetic energy of the pseudo state" when discussing sodium (or Cu) metal; this is a useful concept, as the demonstration shows, but it is not the actual kinetic energy of the bonding electrons.

G. Solt

*Université de Neuchâtel  
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4 December 1985*

<sup>1</sup>V. F. Weisskopf, *Am. J. Phys.* **53**, 940 (1985).

<sup>2</sup>J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), Vol. 1.

<sup>3</sup>V. F. Weisskopf, *Am. J. Phys.* **53**, 304 (1985).

## ON CHEMICAL BONDING

Weisskopf<sup>1</sup> recently published in your Journal a series of publications in which he attempted to devise simple models suitable for didactic purposes. Of course there will always be people who will feel strongly about certain simplifications if they give rise to pre-

dictions which are unrealistic in respects which they consider crucial. I must say that unfortunately I am one of those people. Weisskopf's models allegedly expose the mechanism underlying the formation of chemical bonds as one in which charge concentrates between the nuclei and is attracted by several nuclei in the neighborhood, this attraction being responsible for the observed binding. As a chemist I'm familiar with this view which seems to be quite obvious, which, however, more than half a century ago, has been shown by Slater<sup>2</sup> to be a poor description of reality. The above model for chemical binding suggests that we would have a decrease in the potential energy term of the electronic Hamiltonian as the fragments approach each other from a distance far apart. However, in the case of diatomic molecules, Slater<sup>2</sup> has shown that the potential energy term at first actually increases and that a decrease in the kinetic energy term is responsible for the attraction between the fragments. Incidentally, the investigations by Slater were based on very simple and basic concepts, namely on an assumption concerning the general shape of potential energy curves of diatomic molecules and on the well-known quantum mechanical virial theorem.

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<sup>1</sup>V. Weisskopf, *Am. J. Phys.* **53**, 941 (1985) and refs. therein.

<sup>2</sup>J. C. Slater, *J. Chem. Phys.* **1**, 687 (1933).

## RESPONSE

I am glad that Dr. Solt points out an important fact concerning systems of bound atoms such as molecules, crystals, or metals. In all these cases, the forces are almost purely electrostatic and then a special virial theorem holds which says that the decrease of the to-

tal energy, when going from separate atoms to the bound system, must be accompanied by an increase of kinetic energy of all electrons involved by an amount equal to one half the decrease of the potential energy.

As Dr. Solt correctly points out, the idea of my piece on the metallic bond was to simplify the problem by expressing the complicated interaction of the core electrons with the valence electrons by a pseudopotential. What I called "kinetic energy" is the kinetic energy of the valence electrons only, which become the conduction electrons in the metal. The special virial theorem mentioned above is not fulfilled for an electron in the pseudopotential. Indeed, the flattening of the pseudopotential near the origin is caused by the increase of the kinetic energy of the core electrons when the valence electron is near the core. This is why part of the total kinetic energy (valence plus core) is hidden in the pseudopotential energy. I regret that I did not explicitly point out these relations in my column.

Dr. Senn's letter points out correctly that, when two atoms approach each other in order to form a molecule, the total energy decreases, but the potential and kinetic energies have a more complicated dependence on the distance between the atoms. This was shown in the famous paper by Slater quoted by him. In my derivation of the molecular bond<sup>1</sup> I considered only the total energy so that Slater's statements are irrelevant. It is true that in my discussion of the metallic bond, I consider the potential energy only, but it is the one produced by a pseudopotential to which Slater's conclusions are not applicable, as demonstrated by Dr. Solt's letter.

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23 January 1986*

<sup>1</sup>*Am. J. Phys.* **53**, 399 (1985).

## Search for Simplicity: Chemical energy

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: Chemical energy

Last month we tried to understand the nature of the bond between the atoms in the hydrogen molecule. We saw that the bond occurs because the two electrons merge into a single quantum state similar to the ground state of helium. They are attracted by both nuclei, an effect that is stronger than the sum of repulsions between the nuclei and between the electrons. The binding energy of the hydrogen molecule is 4.6 eV or 106 kcal/mole. Our simplistic approach resulted in 5.7 eV, but there were good reasons for an overestimate.

The merging of two electrons into one state produces what we will call an "electron-pair" bond. Other important examples are the hydrocarbons. In order to understand this, we must first analyze the carbon atom. It has six electrons, two of which occupy the innermost shell (*K*-shell). The other four are in the next shell (*L*-shell) consisting of one *s*-state and 3 *p*-states. In the isolated carbon atom, the *s*-state is doubly occupied and two *p*-states are occupied by one electron. Only little energy is needed to have these four electrons placed into four symmetric states which are linear combinations of the *s*- and *p*-states. These new states have the shape of prongs in the four directions from the center to the corners of a tetrahedron. These are the states that are important for many chemical compounds of carbon. The simplest example is  $\text{CH}_4$ , in which the electron in each prong merges with the electron of a hydrogen atom to form an electron-pair bond, four bonds in all. The total binding energy of  $\text{CH}_4$  is 393 kcal/mole, that is again, about 100 per bond. We use this measure of energy instead of eV because of the round number for the bond energy.

Longer hydrocarbons are also bonded by electron-pair bonds; the two prongs from adjacent carbons merge into a pair bond and the hydrogen electrons merge with the other prongs (see Fig. 1). Again, the binding energy is approximately 100 kcal/mole per bond.

Another related type of bond is found in oxygen compounds. This atom is two electrons short of completing the *L*-shell, which is closed in neon. We can picture the oxygen configuration as a closed shell with two holes. Two of the states are occupied by only one electron. The water molecule is formed when the electrons of the two hydrogen atoms are placed in those holes. This is why we call it a "plug-and-hole" bond. It is related to the electron pair bond since the hydrogen electrons merge with the single electron in the hole and are attracted by both nuclei. Indeed, the total binding energy of water is 222 kcal/mole, that is, 111 per bond, close enough to the pair bond energy.

The two holes in the oxygen atoms are at  $90^\circ$  to each other, if we assume that the outer four electrons are in *p*-states. The three *p*-states can be regarded as dumbbell shaped and oriented at right angles to each other. If we consider the six *L*-shell electrons in the tetrahedral configuration, two prongs would be filled with pairs and two would each have a hole. Then we would get an angle of  $109^\circ$  between the holes. Actually, in the water molecule, the hydrogen atoms are at an angle of  $104^\circ$ . They are definitely on one "side" of the molecule. With the hydrogen electrons sucked into the oxygen holes, the water molecule has an almost closed *L*-shell of total charge minus two on one side and two positive protons on the other, giving rise to a strong dipole moment. This is what makes water such a strong dielectric and consequently an excellent solvent.

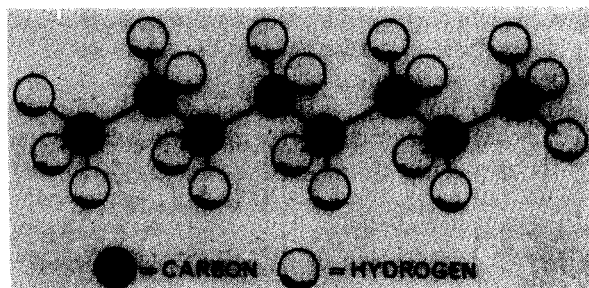


Fig. 1. Chain of atoms in a hydrocarbon (Octane,  $\text{C}_8\text{H}_{18}$ ) linked by tetrahedron bonds.

Life is based on that property.

Another important oxygen compound is  $\text{CO}_2$ . It is more difficult to understand with our simple pictures that the four bonds are of the "plug-and-hole" type. One may assume that the four prongs of C are "bent" so that they fit into the two holes at each O atom. We then get a molecule with C at the center flanked on both sides by oxygen atoms. The total binding energy is 385; that is again, about 100 kcal/mole per bond.

A third type is the ionic bond. A typical example is NaCl. It is usually explained by saying that the negative electrostatic attraction energy of the  $\text{Na}^+$  and  $\text{Cl}^-$  ion adjacent to one another, is greater than the positive energy needed to transfer an electron from the Na atom to the Cl atom. That this should be indeed so can be seen by the following consideration (see Fig. 2). Sodium consists of a closed shell with one relatively loosely bound electron outside, which spreads over a sphere with a radius, say, of about twice that of the closed shell. The chlorine is a closed shell with a hole in it. Let us put the two atoms together so that the closed shells touch. This should not take much energy since they are neutral. To press them together more than that would cost much energy because closed shells cannot penetrate except at the cost of lifting electrons to higher states, because of the Pauli principle. Now we put the outer electron of sodium into the hole of the chlorine. To do this we do not need to work against the binding of that electron to the sodium core, since the average position of the hole is about as far from the sodium center as the electron has been in the atomic state, that is, about two core radii. But, we gain the electron affinity of chlorine, that is, the energy gained by putting an electron into the hole, where it is attracted by the chlorine nucleus. Thus the binding energy of the NaCl molecule ought to be roughly near to the electron affinity of chlorine. We expect it to be of the order of a pair bond since the electron merges with the

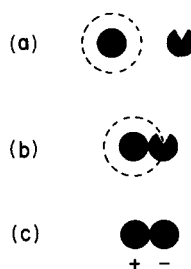


Fig. 2. (a) Shows the Na and Cl atoms. The former is surrounded by the valence electron, the latter with a hole. (b) The cores touch; the energy of (a) and (b) are about equal. (c) The valence electron entered the hole which is, on the average, at the same distance from the Na center as the electron in the isolated atom. The energy of (c) is lower than (a) by about the electron affinity of Cl.

single electron in the hole. Indeed, the affinity of Cl is 84 kcal/mole, the binding energy of the NaCl molecule is 98 kcal/mole, and that of KCl is 102 kcal/mole. In the cases of fluorine compounds the binding energy deviates more from the electron affinity of F. The latter is 80 kcal/mole, whereas the binding energy of NaF is 115, and that of KF is 120 kcal/mole. This is because the core of F is smaller than the core of Cl so that the electron filling the hole of F is nearer to the core of Na or K in the molecule than it is in the isolated Na or K atoms. We see that the ionic bond also yields bindings of the order of 100 kcal/mole.

The electron-pair bond, the ionic, and the plug-and-hole bond are "strong" bonds of about 100 kcal/mole. There are also medium bonds in the region of 20–60 kcal/mole. Examples are "hindered" electron-pair bonds such as  $\text{Li}_2$  or  $\text{Na}_2$ , binary compounds of atoms whose valence electrons form a pair-bond, but the cores get in the way and weaken it. Other medium bonds are  $\text{F}_2$ ,  $\text{O}_2$ , and  $\text{Cl}_2$ , pairs of atoms with one or two holes in a closed shell. "Hole-hole" bonds are not so strong. The most important of these is  $\text{O}_2$  whose binding energy is 118 kcal/mole; this is only 59 per bond.

Let us now apply our knowledge to the energy gain in combustion. What happens in combustion? Oxygen molecules in air are split and their atoms are incorporated in stable compounds, mostly carbon dioxide and water. The oxygen atoms leave medium bonds and enter into strong bonds. Therefore the energy gain in combustion should be the difference between a strong and a medium bond, roughly, 40–50 kcal/mole, per oxygen atom taken from the air.<sup>1</sup>

Let us burn methane, the main constituent of household gas:  $\text{CH}_4 + 2 \text{O}_2 = \text{CO}_2 + 2 \text{H}_2\text{O}$ . Two oxygen molecules of air are used for the combustion of our molecule methane. Thus four medium bonds are broken and replaced by strong bonds in water and  $\text{CO}_2$ . Hence we should get 160–200 kcal for burning one mole of methane. The actual value is 190 kcal.

What about gasoline? It is a hydrocarbon chain as shown in Fig. 1. Consider one  $\text{CH}_2$  link:  $\text{CH}_2 + 3/2 \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$ . We should gain three times the difference, which is 120–150 kcal/mole of  $\text{CH}_2$ , or 9–11 kcal per gram. Actually, it is 10 kcal/g.

The third example is glucose:  $\text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{O}_2 = 6 \text{CO}_2 + 6 \text{H}_2\text{O}$ . The gain is 12 times the difference: 480–600 kcal/mole. The correct value is 590 (honey) which means  $1.38 \times 10^{11}$  ergs/g.

Let us use this result to estimate how long a bee can fly on one milligram of honey, the result of sucking a few flowers. The bee does not fly like an airplane using the air flow passing by, but keeps itself suspended almost at rest, not unlike a helicopter. It produces a stream of air downwards to compensate for gravity. We will show next time that the power needed to keep the bee in the air is  $(mg)^{3/2}/(\sigma\rho)^{1/2}$ , where  $m$  is the mass of the bee,  $\sigma$  the area of the wings, and  $\rho$  the density of air. It is about  $1.8 \times 10^3$  ergs/s, using  $m = 10^{-2}$  g and  $\sigma = 0.3$  cm<sup>2</sup>. A milligram of honey, therefore, lasts for a few hours, counting with an efficiency of biological metabolism for mechanical work of 10% to 15%.

Another question is the amount of food needed for a person just to keep warm. Enrico Fermi started this estimate with the remark, "I know from reading mystery novels that a corpse needs about half a day to cool from body temperature to room temperature." Assuming a weight of 60 kg, we get from this information that the body needs about 2000 kcal per day to stay at body temperature; this is 100 W. Assuming all food is roughly as nourishing as honey, we find it needs about 600 g of food per day. Here we can count on full efficiency since all losses produce heat. This amount of energy would lift the person to 1.5 times the height of Mt. Everest, not counting metabolic and other losses incurred when climbing. It shows how much harder it is to produce heat than mechanical energy. Note that the human body produces 1.7 mW per gram, whereas the sun produces only  $2 \times 10^{-7}$  W per gram!

Now to the question left open in the last essay. Two hydrogen atoms are held at a distance  $\rho$  between the protons. The energy  $E$  goes to infinity when  $\rho$  is made to approach zero, because of the electrostatic repulsion between the protons. In the helium atom, this repulsion is more than compensated for by the nuclear forces within the helium nucleus. We are not interested in the energy of the helium nucleus, but only in the energy of the electron configuration. The latter energy is  $E' = E - e^2/\rho$ . It is that energy which equals the energy  $-5.85$  Ry of the electrons in the helium atom for  $\rho = 0$ .

Victor F. Weisskopf

<sup>1</sup>E. Purcell mentions that fact in his column, "The Back of the Envelope," which appeared in the April 1984 issue of this journal.

## Search for Simplicity: The size of molecules revisited

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: The size of molecules revisited

This contribution contains corrections and additions to the January, 1985 installment of "Search for Simplicity" and the promised computation of the power needed to keep a bee in the air. I owe a great debt to Professor N. O. Murchadha from the Physics Department of the University College in Cork, Ireland for pointing out errors in that essay and for a hint as to how to explain a question I raised. I tried to determine the distance between molecules or atoms in liquids by comparing the surface tension and the binding energy  $\epsilon_B$  of the constituents. I wrongly equated  $\epsilon_B$  with the heat of evaporation plus the energy necessary to heat the liquid from the temperature  $T_s$ , at which the surface tension was measured, to the boiling point  $T_b$  at atmospheric pressure. I forgot to subtract the work against the air pressure.

I reproduce here Dr. Murchadha's letter with a few omissions and with different symbols in order to adjust it to the ones I used. I also changed some of the numbers in his table because they were based upon my figures in which I discovered a few inaccuracies. I added the values for a few metals in their liquid state, and the temperatures  $T_s$  and  $T_b$ , as defined above. The symbol  $\delta$  stands for the energy needed to raise the temperature of the liquid from  $T_s$  to  $T_b$ . In the computation of  $\delta$  the specific heat of liquids was approximated by 6 cal/mole except for water, where it is 18 cal/mole.

Following is Dr. Murchadha's letter:

Dear Sir:

In an illuminating article [Am. J. Phys. 53, 19–20 (1985)], V. F. Weisskopf derives an expression relating the distance  $d$  between molecules in a liquid to the surface tension  $S$  and the molecular binding energy per unit volume  $\epsilon_B$  as

$$d = \frac{6S}{\epsilon_B}. \quad (1)$$

He applied this formula to four liquids and obtained a satisfactory agreement between theoretical prediction and observation. I wish to claim that this agreement, and particularly the fact that the theoretical values are consistently less than the observed values, is suspect. The problem is that one must distinguish between latent heat

and binding energy. When we boil a liquid the vapour expands and can do work on the surroundings. We must subtract this " $P dV$ " work from the latent heat to get the true binding energy  $U$  at the boiling point. (Technically, the latent heat is the change in enthalpy  $\Delta H = U + PV$ , and we must subtract of the change in  $PV$  to get the change in  $U$ .)

If we assume that the volume of the liquid is negligible in comparison to the volume of the vapour and that the vapour is an ideal gas, it is easy to see that the subtracted term is  $RT$  per mole. This term, in the case of each of the four liquids analysed by Professor Weisskopf, is about 10% of the latent heat. (The constancy of this ratio can be justified on thermodynamic grounds.) Working in the units of Professor Weisskopf, I would suggest replacing his table with a new one.

As Professor Weisskopf states, it is easy to understand situations where the predicted value is less than the actual value. One explanation for a predicted value larger than the actual value is the existence of long-range forces in the liquid. The surface layer loses a sixth of its binding energy, but the second layer can also lose some energy, so the total loss of energy can be greater than one-sixth, demanding a coefficient in the equation larger than six. The neon result, for example, could be rationalised by demanding a binding second-neighbour term in the potential of the order of 20 of the nearest-neighbour effect.

Could it be that this also is an explanation for the large deviations Professor Weisskopf observes with the molten metals? To get large deviations we have to demand that long-range terms in the binding energies are comparable to the nearest-neighbour effects. This does not seem totally unreasonable for metals. [see Table I.]

Dr. Murchadha is right. A correct calculation shows that the calculated distance is smaller than the actual one only for water and aluminum; in six other cases they agree within 10% and in three cases they are about twice as large. Dr. Murchadha found the explanation of the question I could not answer: How could the surface tension be larger than  $(\frac{1}{6}) \epsilon_B d$ ? (Please replace  $d^{-2}$  by  $d$  in the last paragraph of my January article.) Let me express his idea as follows: If we take into account the interactions not only with the six nearest neighbors but also with the 20 next nearest neighbors in a cubic arrangement (see Fig. 1), then the surface atoms lose not one partner out of six but nine out of twenty-six! Thus the ratio of the loss of binding at the surface to

Table I. Relevant values for ten liquid materials and the resulting distances  $d$  compared with the actual values. Sources: *American Institute of Physics Handbook* (1972), 3rd ed.; *CRC Handbook of Chemistry and Physics* (1977), 58th ed.

	H <sub>2</sub> O	C Cl <sub>4</sub>	Ne	Ar	Al	Fe	Cd	Cu	Hg	Ag
$S$ in ergs/cm <sup>3</sup>	73	27	5.5	13.2	840	1720	630	1880	470	920
$T_s$ in K <sup>0</sup>	293	293	25	85	973	1810	594	1360	292	1240
$\delta H$ in 10 <sup>9</sup> ergs/cm <sup>3</sup>	23	3.1	1.1	2.3	257	439	71	371	40	216
$T_b$ in K <sup>0</sup>	373	350	27	87	2793	3135	1040	2839	630	2436
$RT_b$ in 10 <sup>9</sup> ergs/cm <sup>3</sup>	1.8	0.3	0.13	0.26	20	33	6.1	29	3.5	17
$U$ in 10 <sup>9</sup> ergs/cm <sup>3</sup>	21	2.8	0.97	2.04	237	406	65	342	36.5	199
$\delta$ in 10 <sup>9</sup> ergs/cm <sup>3</sup>	3.4	...	...	...	40	41	8	46	5.7	26
$\epsilon_B$ in 10 <sup>9</sup> ergs/cm <sup>3</sup>	24	2.8	0.97	2.04	277	447	73	388	42	225
$d$ from Eq. (1) in 10 <sup>-8</sup> cm	1.9	5.8	3.4	3.9	1.8	2.3	5.2	2.9	6.7	2.5
$d$ , actual value in 10 <sup>-8</sup> cm	3.2	5.4	3.1	3.6	2.7	2.4	2.9	2.4	2.9	2.7



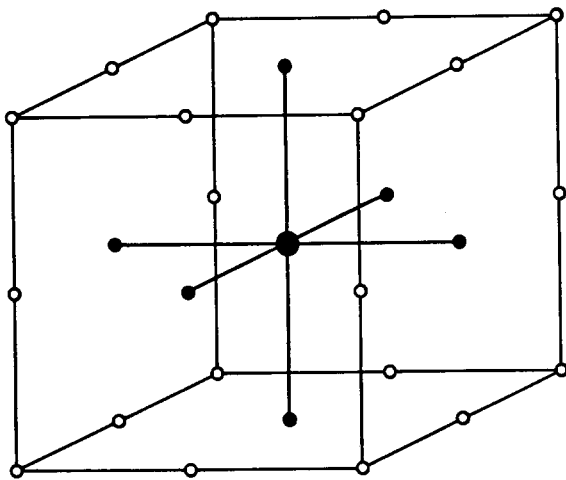


Fig. 1. The nearest neighbors (●) and the next nearest neighbors (○) of the center of a cubic arrangement.

that in the interior may be larger than  $\frac{1}{8}$ , even if the interactions with the next to nearest neighbors are weaker.

I owe the readers a derivation of the power needed to keep a bee in the air. The bee is pulled downwards by the force  $mg$ , where  $m$  is its mass. To counter this force the bee

produced a column of air of a cross section of  $\sigma \text{ cm}^2$  moving downwards with a velocity  $v$ . Roughly speaking,  $\sigma$  is the area of the wings. The momentum of 1 cm of that column is  $\sigma \rho v$ , where  $\rho$  is the density of air. In one second the bee produces an air column of length  $v$ , so that the down momentum produced per second is  $\sigma \rho v^2$ . A momentum per second is a force; it balances the gravity force so that we get  $\sigma \rho v^2 = mg$ , or  $v^2 = mg/\sigma \rho$ . The power  $P$  needed to produce that air stream is the force times the velocity.  $P = mgv = (mg)^{3/2}(\sigma \rho)^{1/2}$ . This was the expression used last month.

It is interesting to estimate the wing-beat frequency. In order to produce an air flow with a speed  $v$ , the wing speed must be of the same order. The vibrational amplitude is about  $\sigma^{1/2}$  so that we get for the frequency<sup>1</sup>  $\nu \sim v/\sigma^{1/2} \sim (mg/\rho)^{1/2}/\sigma$ . With  $m \sim 10^{-2} \text{ g}$  and  $\sigma \sim 0.3 \text{ cm}$ , we obtain  $\nu \sim 2 \times 10^2 \text{ cm/s}$  and  $\nu \sim 300 \text{ s}^{-1}$ , which corresponds roughly to the pitch of a tone in the middle of the piano. This is the hum we hear in midsummer lying in a meadow full of flowers.

Victor F. Weisskopf

<sup>1</sup>A similar formula was derived by B. Corben, J. Theor. Biol. **102**, 611 (1983).

## PROBLEM

A solid with plane boundary is swinging on the outside of a fixed cylinder of any convex shape.

Let us define  $\mathbf{r}(s)$  the radius vector connecting the center of mass  $G$  of the swinging solid to the contact point  $M$ ,  $\mathbf{n}(s)$  is the inner normal to the cylinder cross section,  $s$  is the curvilinear coordinate ( $s = 0$  corresponds to the equilibrium at a point  $M_0$ ),  $\|\mathbf{r}(0)\| = GM_0 = h$ ,  $m$  is the swinging

mass,  $k^2$  is the radius of gyration around  $G$ , and  $g$  is the gravity constant.

Let us compare this motion with the "opposite" one where a solid of the *same shape* (with same  $m, k, h$ ) is rolling on a horizontal plane. Prove that for small oscillations, the period is the same; but for large oscillations, the period is different. (Solution is on page 693.)

## Search for Simplicity: The cohesive energy of solids

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: The cohesive energy of solids

How much energy is needed to remove an atom or molecule from the interior of a solid? Call this energy  $\epsilon_B$ . Then  $N\epsilon_B$  is the energy required to decompose a solid of  $N$  atoms or  $N$  molecules into  $N$  separate atoms or molecules. In these considerations, the atoms at the surface are neglected ( $N \gg 1$ ).

We will consider three types of solids: covalent crystals such as diamond, ionic crystals such as NaCl, and metals. The treatment of metals will be taken up next month. Let us start with diamond. A "covalent" bond is what we have called "electron-pair" bond. The carbon atom is very suitable for forming a solid by electron-pair bonds when it is in the state where the four outer electrons are in the configuration forming prongs in the four directions from the center to the corners of a tetrahedron (see Ref. 1). Figure 1 shows that it is possible to arrange the carbon atoms such that always two prongs of two neighbors merge and form an electron-pair bond. There are two bonds per atom, although four bonds emerge from each atom; each bond belongs to two atoms.

As we saw in Refs. 1 and 2, an electron-pair bond is worth about 100 kcal/mole of binding energy. So we expect  $\epsilon_B$  for diamond to be about 200 kcal/mole. Actually it is 171; this is near enough for such crude approximations.

Here is the place to improve our conclusions of Ref. 1, in which the search for simplicity was a little overstretched. We remarked that "only a little energy is needed" to place four electrons from the atomic groundstate into the configuration of four prongs directed to the corners of a tetrahedron. Actually the energy to do so is about 7.5 eV or 170 kcal/mole. This amount is not small; it is almost equal to the cohesion energy of the carbon atom in diamond, and 1.6 times the bond energy of the hydrogen molecule. Why, then, is the energy per bond near 100 kcal/mole—about the same as in  $H_2$ —in molecules such as  $CH_4$ ,  $CO_2$ ,  $H_2O$ ; in hydrocarbons; and in diamond, although the "expensive" tetrahedral configuration must be formed before merging of electron pairs can take place? We described the water molecule also by assuming that the six outer electrons in oxygen are in the tetrahedral configuration, two prongs being occupied doubly; the other two merge with the H atoms.

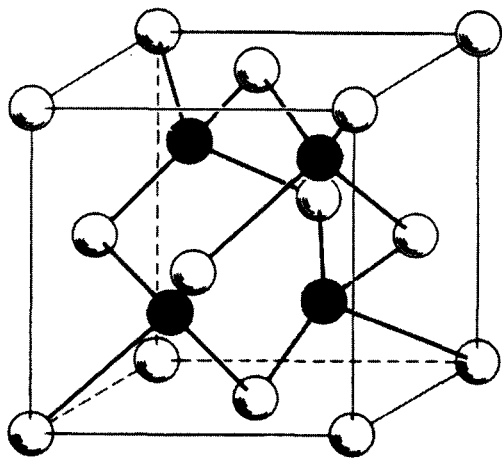


Fig. 1. Diamond lattice. The shaded circles are those carbon atoms that have all their nearest neighbors in the figure.

There must be a compensating effect which makes the bond energy larger than in  $H_2$ . Indeed this is the case. Remember that the  $H_2$  bond comes about because the two electrons are attracted by both nuclei. This attraction is stronger than the repulsion between the nuclei and between the electrons. In the case of carbon-hydrogen or oxygen-hydrogen bonds, one of the nuclei has a larger charge, which is only partially reduced by the electron clouds surrounding it. In the case of  $CO_2$ , in the C-C bonds of hydrocarbons, and in diamond, both nuclei participating in the bonds have a larger charge. This increases the bond strength relative to the  $H_2$  bond. We cannot prove quantitatively why this effect compensates almost exactly the energy needed to establish the tetrahedral configurations in the molecules and solids considered here, but we can at least understand the presence of a compensating effect.

What about ionic crystals? In Ref. 1 we discussed ionic molecules such as NaCl, and we found a reason that the cost of formation of a positive Na ion and a negative Cl ion is more than compensated by the gain in energy due to their Coulomb attraction. This is true, even to a greater extent, in the NaCl crystal.

The alkali-halide crystals are made up of ions, not of atoms; of the positive ions of the alkali metal such as  $Na^+$ ; and the negative ones of the halogens such as  $Cl^-$ . We therefore start by determining the energy needed to decompose the crystal into separate ions. Each ion consists of a closed electron shell; in  $Na^+$  and  $F^-$  it is the neon configuration and in  $K^+$  and  $Cl^-$  it is the argon configuration. Such closed shells act almost like rigid spheres; the electrostatic attraction between the ions produces only very little compression of the shells. We therefore consider them as approximately rigid. The electrostatic attraction keeps the ion as close as possible, that is, the distances at which the "rigid" shells touch. It is not easy to determine the radii of these shells from first principles. Let us get them from the known density  $\rho$  (grams per  $cm^3$ ) of the crystal. The sum of the radii of the two different ions (that is all we will need) must be equal to the distance  $d$  between nearest neighbors. It is easy to see that  $d = (A/L\rho)^{1/3}$ , where  $A$  is the average atomic weight of the two atoms (29.2 for NaCl) and  $L$  is Avogadro's number.

The next problem is the determination of the energy of the electrostatic attraction which must be overcome when the lattice is decomposed. An ion is attracted by its six nearest neighbors (see Fig. 2); it is repelled by ions of the same charge at a larger distance but attracted again by opposite ions further away. The attraction wins out; the total energy of one ion is  $-ae^2/d$ , where  $a$  is the so-called "Madelung" constant;  $a = 1.75$  for this kind of lattice. The attractive energy is almost twice the energy of a single pair at a distance  $d$ . The repulsion between the ion shells does not contribute to the energy in our approximation since we assumed them to be incompressible.

Under these assumptions, the energy needed to decompose a crystal composed of  $N$  ions into separate ions would be  $N\epsilon_B^* = \frac{1}{2} Nae^2/d$ . The factor  $\frac{1}{2}$  comes from the fact that each interaction between two ions contributes to the binding energy of both ions. It therefore must be multiplied with  $\frac{1}{2} N$  to get the total.

In order to get the energy  $N\epsilon_B$  needed to decompose the

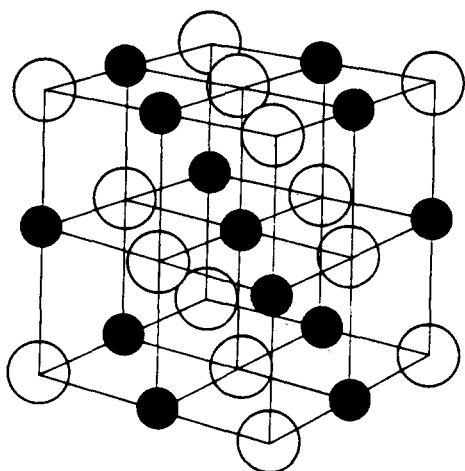


Fig. 2. NaCl lattice. Closed circles are positive ions; open circles are negative ions.

crystal into separate atoms we must subtract the energy gained by transferring an electron from the negative to the positive ion. It is the difference  $\delta$  between the ionization energy of the alkali atom and the electron affinity of the halogen:  $\epsilon_B = \epsilon_B^* - \frac{1}{2}\delta$ . The factor  $\frac{1}{2}$  appears because one transfer makes two atoms from two ions.

Table I gives the values of  $d$ , the calculated energies  $\epsilon_B^*$  and  $\epsilon_B$ , and the actual cohesion energies  $\epsilon_B$  for a few alkali-halides. (The actual values are taken from Ref. 3.)

The calculated values of  $\epsilon_B$  are all larger than the actual ones by 10%–15%. This is a consequence of our assumption of incompressible ions. Actually the ions are compressed, which raises their energy. This effect is rather small since the ions are configurations of electrons packed tightly, resisting compression like an electron gas of several electrons within the volume of the ion (see remarks at the end of Ref. 4).

Altogether we conclude that ionic crystals have binding energies per atom of roughly 80 kcal/mole within 15% of

Table I. The lattice distances, the calculated, and the actual binding energies of alkali-halides (distances in  $10^{-8}$  cm, energies in kcal/mole).

	NaF	NaCl	NaBr	KF	KCl	KBr
$d$	2.39	2.82	2.99	2.69	3.15	3.30
$\epsilon_B^*$ (calc)	122	103	98	108	92	88
$\epsilon_B$ (calc)	102	85	77	97	84	78
$\epsilon_B$ (actual)	88	75	67	86	77	68

this value. This binding is considerably stronger than the bond of an atom in a molecule. The molecular bond between an alkali and halogen atom was found to be of the order of 90 kcal/mole, but this bond involves two atoms and, therefore, must be compared to a binding of about 160 kcal/mole in the crystal.

As we have seen, the attractive electrostatic energy of an ion in the lattice is  $\alpha$  times larger than the same energy of two ions at the distance  $d$  of the nearest neighbors in the lattice; here  $\alpha$  is the Madelung constant ( $\alpha = 1.75$  for the lattices considered here). In our approximation of rigid ions,  $d$  is also the distance between the ions in the molecule. Thus the binding energies in the solid are  $\alpha$  times larger than in the molecule. That is why the crystal is a stable configuration at ordinary temperatures. When the temperature exceeds the melting point, the heat energy destroys the orderly arrangement of the crystal. At the boiling point the heat energy decomposes the crystal into molecules. These phenomena will be taken up in a later essay.

Victor F. Weisskopf

<sup>1</sup>V. Weisskopf, Am. J. Phys. **53**, 522 (1985).

<sup>2</sup>V. Weisskopf, Am. J. Phys. **53**, 399 (1985).

<sup>3</sup>C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), 5th ed.

<sup>4</sup>V. Weisskopf, Am. J. Phys. **53**, 109 (1985).

## Search for Simplicity: The metallic bond

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: The metallic bond

This essay is devoted to the cohesion energy of metals. Metals are formed by atoms which, when isolated, have one, two, or three loosely bound outer electrons, whereas the rest of the electrons form a tightly bound core. When such atoms assemble in a metal, the cores form a regular lattice of positive ions and the outer electrons—the conduction electrons—move all over the lattice more or less as free particles. This “free-motion” is based upon a typical quantum effect derived from the wave nature of the electrons: A plane wave generally is not much altered when it penetrates a regular array of obstacles. A typical example is the transparency of crystals to light waves. Crudely speaking, all that changes is the relation between frequency and wavelength or between energy and momentum. Therefore, the motion of an electron in a metal can be approximately considered as a free-motion, but sometimes an “effective” mass  $m$  different from the electron mass  $m$  must be introduced. Only deviations from the regular lattice array produce a scattering of the waves. Such deviations occur, for example, by thermal fluctuations. The ensuing small deviations from free-motion cause the electric resistivity of metals, a topic which will be treated in a later installment.

We will consider here only metals with one conduction electron per atom: in particular, sodium and copper. The simplest metal, one may think, would be formed by hydrogen. This is, however, not the case under normal pressures. The reason lies in the relatively strong bond (13.6 eV) of the electron to the atom. It is instructive to show why no hydrogen metal exists by calculating the energy per atom in a metallic configuration. This energy is not low enough compared to that of an isolated atom.

Consider the metal as a cubic lattice of positive ions (protons) in which there is a gas of free-electrons, one per ion. In our simplified consideration, this gas represents a uniform negative charge distribution of one unit  $-e$  of charge per cell. A cell is a cube of side length  $d$  with a proton in the center. Let us determine the electrostatic energy. We neglect the effect of all neighboring cells because the total charge in each cell is zero in the average. We approximate the cubic cell by a sphere of equal volume whose radius is  $r_s = (3/4\pi)^{1/3}d$ . (See Fig. 1.) The electrostatic energy  $V$  of a negative charge  $-e$  distributed uniformly over the sphere

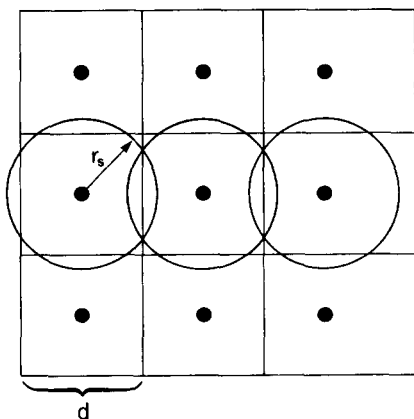


Fig. 1. Cubic lattice. The cubic cells around the ions (black circles) are replaced by spheres of radius  $r_s$ .

and a positive point charge at the center, is  $V = -1.5e^2/r_s$ . Now we must add the kinetic energy. In the February installment<sup>1</sup> we have learned about the minimum kinetic energy of a free-electron gas with one electron in the average per  $d^3$  [Eqs. (3) and (4)]. Replacing  $d$  by  $r_s$ , we get for the kinetic energy  $K$  of one electron

$$K = 2.21(\hbar^2/2mr_s^2). \quad (1)$$

The total energy per cell is  $E = V + K$ . This sum has a minimum for  $r_s = 1.47a_B$  ( $a_B$  is the Bohr radius) and a corresponding energy  $E = -1.02Ry$ . These figures are arrived at by using Eqs. (3) and (4) from the April installment.<sup>2</sup> A more detailed calculation, taking into account the deviations from a free-electron gas and the interactions between the electrons, gives  $E = -1.05Ry$ . This shows that our primitive approach is not much off the calculation.

This energy is slightly lower than the  $-1Ry$ , the energy of the isolated atom. However, the hydrogen metal is not stable because the isolated atoms would form a gas of molecules. The molecular bond is  $0.34Ry$  (see Ref. 3) or  $0.17Ry$  per atom. Thus it pays to form a molecular gas instead of a metallic lattice. At very low temperatures the  $H_2$  molecules form a regular array due to the weak intermolecular forces. It is not a metal since the electrons are strongly bound in the molecules.

Why are metals different from hydrogen? Let us begin with sodium. The Na atoms consists of an inner core, a closed shell of ten electrons, and a single outer electron which is bound by the ionization energy  $I = 0.378Ry$  instead of  $I = 1Ry$  in hydrogen. We intend to describe the effect of the core on the outer electrons in terms of a potential energy function  $U(r)$ , usually referred to as “pseudopotential.” Outside the core radius, it is a Coulomb field of the core charge  $+e$ . Inside there are two effects acting on the electron. One is an increased attraction and the other is the effect of the Pauli principle allowing the electron to penetrate the core only at a cost: It must get into unoccupied quantum states within the core (see remarks at the end of Ref. 4).

The simplest way to take these effects into account is to choose a Coulomb potential for  $r > r_0$  and let it become constant at  $r < r_0$ :

$$U = -(e^2/r) \text{ for } r > r_0, \quad U = -(e^2/r_0) \text{ for } r < r_0, \quad (2)$$

as shown in Fig. 2. Note that  $r_0$  is not really the core radius. It is the radius of the region of constant potential energy  $-e^2/r_0$ , which simulates the effect of the core. The actual core radius is likely to be smaller. We find the value of  $r_0$  by solving the Schrödinger equation for the lowest state in the potential (2) and adjust  $r_0$  such that the energy of that state is the negative of the observed ionization energy  $I$  of sodium. A simple computer calculation gives  $r_0 = 3.26a_B$ .

Now we are able to determine the sodium lattice energy and distance. We again assume a free-electron gas with a kinetic energy (1) per electron. The average potential energy  $V$  is easy to calculate with a uniform electron density  $\rho = 1/d^3$  and the potential (2). The result for the sum  $V + K = E$  is

$$E = -\frac{3}{2} \frac{e^2}{r_s} + \frac{1}{2} \frac{r_0^2 e^2}{r_s^3} + 2.21 \frac{\hbar^2}{2mr_s^2}. \quad (3)$$

The minimum of (3) is at  $r_s = 4.08a_B$ , which compares fa-



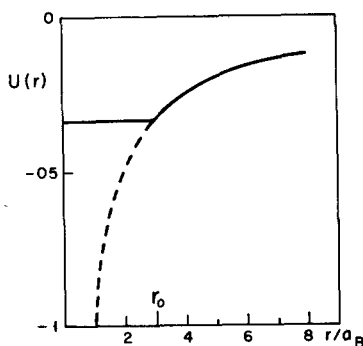


Fig. 2. The pseudopotential  $U(r)$  in units of  $Ry$ . It is a Coulomb potential  $-e^2/r$  outside  $r_0$  and constant within  $r_0$ . The dashed line is the continuation of the Coulomb potential.

vorably with the actual value  $r_s = 4.00a_B$ . The energy (3) for  $r_s = 4.08a_B$  is  $-0.446Ry$ , which is lower by  $0.068 Ry = 0.93 \text{ eV}$  than the energy of the isolated atom. The actual energy needed to free a sodium atom from the lattice is  $1.11 \text{ eV}$ . Now we must make sure that it would not pay to separate the Na atoms and form a molecular gas. The binding of the Na molecule is  $0.8 \text{ eV}$ , that is,  $0.4$  per atom, less than half the binding in the lattice.

This method of determining the lattice distance  $d = (4\pi/e)^{1/3}r_s$  and the binding energy  $E$  is the same, in principle, as the one used to determine the radius and energy of the hydrogen atom in Ref. 4. The two magnitudes are determined by the equilibrium between the attractive force given by (2) and the Schrödinger force; the latter is repulsive and tends to decrease the kinetic energy.

Let us apply the same method to copper. The ionization energy of copper is  $0.57Ry$ . A computer calculation shows that  $r_0 = 1.65a_B$  for the lowest state in the potential (2) to be  $-0.57Ry$ . With this value of  $r_0$  the minimum of (3) occurs when  $r_s = 2.54a_B$  and  $E = 0.67Ry$ . This would give rise to a binding energy in the metal of  $0.1Ry = 1.4 \text{ eV}$ , less than the observed  $3.5 \text{ eV}$ . But in copper the electron gas is not as free as in sodium. Indeed, the properties of the electron gas in Cu can be described by introducing an effective mass  $m^* \sim 1.5m$ . This makes the kinetic energy smaller; the last term in (3) should be reduced by a factor  $m/m^*$ . Then the minimum of (3) gives  $r_s = 2.21a_B$  and  $E = -0.80Ry$ , leading to a binding energy of  $0.23Ry = 3.1 \text{ eV}$  reasonably close to the actual value of  $3.5 \text{ eV}$ . The observed value of  $r_s$  is  $2.7a_B$ , which is  $25\%$  larger than the calculated one.

What is the physical interpretation of the metallic bond? Why do metal atoms form solids and hydrogen not? We will answer these questions in the simplest possible way for metals with one conduction electron per atom. We make use of the free-electron gas approximation implying a uniform charge density of electrons, and the simple pseudopotential  $U(r)$  given by (2).

Figure 3 shows the electron density  $\rho_a$  of the Na atom and  $\rho_m$  of the metal in a cell around a given ion. Both densities add up to one unit when integrated over all space in the case of the atom, and over the cell volume (a sphere of radius  $r_s$ ) in the case of the metal. When we go from the atom to the metal, the electron distribution changes in two ways: (1) the charge in the peak near  $r = 0$  (cross hatched in Fig. 3) is moved to regions of the cell further out where  $\rho_m > \rho_a$ ; (2) the charge outside  $r_s$  is moved to inside  $r_s$ . The first change should be executed such that the peak charge is

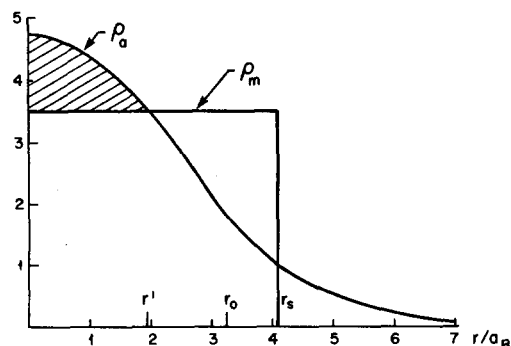


Fig. 3. The electron density  $\rho_a$  in the sodium atom and  $\rho_m$  in the metal. The units are  $10^{-3} a_B^{-3}$ .

transferred to the region between  $r'$  and  $r_0$ , where  $r'$  is the radius beyond which  $\rho_a$  is less than  $\rho_m$ . (There is enough space in that region because it is a spherical shell.) The second change fills in the rest of  $\rho_m$ . It is easily seen that the potential energy is decreased. The first change does not alter it since  $U$  is constant between  $0$  and  $r_0$ ; the second change lowers the potential energy since  $U$  is lower inside of  $r_s$  than outside. It turns out that the kinetic energy (1) of the metal and that of the electron in the atom are practically the same. Thus the total energy is lower in the metal than in the isolated atom. If  $m^* > m$  as in Cu, the kinetic energy of the metal is also lowered; this contributes to the bond.

Why is it not so in hydrogen? Figure 4 shows the corresponding situation. The potential  $U(r)$  is  $-e^2/r$  all the way to the center. This has two consequences: First, the cross-hatched peak is much larger; second, the transfer of the peak to the uniform metallic density increases the potential energy since  $U(r)$  has no flat region as in the metallic case. This increase almost cancels the decrease due to the transfer of the charge from outside  $r_s$ . The kinetic energies again are about equal so that no binding results.

How do we interpret the main effect causing the metallic binding: the transfer of the atomic charge outside of  $r_s$  to the region inside  $r_s$ ? Let us call this charge the "tail of the atoms." If we put isolated sodium atoms together to form a

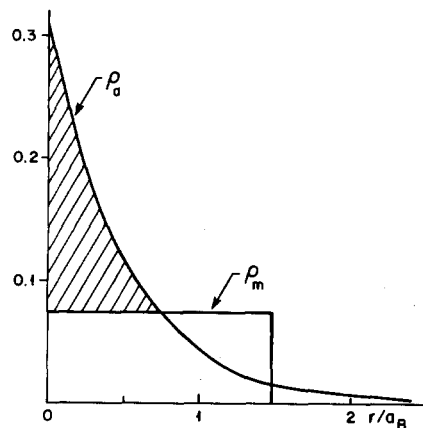


Fig. 4. The electron density  $\rho_a$  in hydrogen and  $\rho_m$  in the hypothetical hydrogen metal.

metal, the tails of neighboring atoms overlap with the charge distribution of a given "central" atom and transform its  $\rho_a$ , a decreasing function of  $r$ , into the constant function  $\rho_m$ . In other words, parts of the electrons of the neighboring atoms get into the cell of the central atom and are attracted by the central core. This is responsible for the increased binding. Thus the metallic bond comes from the fact that each electron is attracted by more than one ion. Qualitatively speaking it is the same mechanism that

causes the molecular bond (see Refs. 3 and 5).

Victor F. Weisskopf

<sup>1</sup>V. Weisskopf, Am. J. Phys. **53**, 109 (1985).

<sup>2</sup>V. Weisskopf, Am. J. Phys. **53**, 304 (1985).

<sup>3</sup>V. Weisskopf, Am. J. Phys. **53**, 399 (1985).

<sup>4</sup>V. Weisskopf, Am. J. Phys. **53**, 206 (1985).

<sup>5</sup>V. Weisskopf, Am. J. Phys. **53**, 522 (1985).

## PROBLEM: THE NATURAL FREQUENCY OF A VIBRATING PARTICLE CONNECTED TO $N$ ARBITRARY SPRINGS

**PART A.** Consider the system shown in Fig. 1 in which a particle of mass  $m$  is connected to an arbitrary number of  $n$  linear springs, each having a spring constant  $k_i$ ; ( $i = 1$  to  $n$ ).  $x$  and  $y$  are the coordinates of the particle. The system is constructed so that the stretch of each spring is the distance

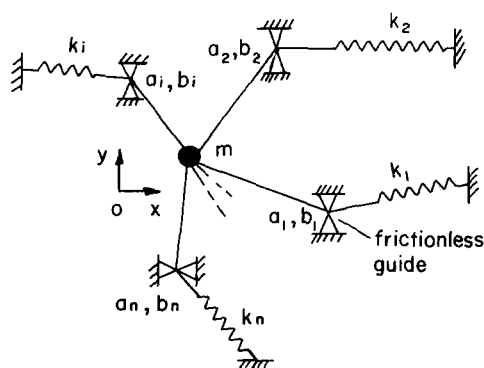


Fig. 1. A system whose springs have zero effective unstretched length.

from  $m$  to the corresponding point  $a_i, b_i$ ; ( $i = 1$  to  $n$ ). Hence the effective unstretched lengths of the springs are zero. Describe the motion of the system. Compare the results with the system considered in part B.

**PART B.** The system shown in Fig. 2 consists of a particle of mass  $m$ , connected to  $n$  springs having different constants. The springs are unstretched when the  $x$  and  $y$  coordinates of  $m$  are zero. Note that unlike part A the springs have a finite unstretched length. Describe the motion of the system for small  $x$  and  $y$ . (Solution is on page 1009.)

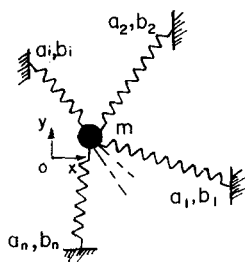


Fig. 2. A system whose springs have a finite unstretched length.

## Search for Simplicity: Thermal Expansion

Victor F. Weisskopf and Herbert Bernstein

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## ADVERTISEMENT



The length  $L$  of a rod of solid materials increases with rising temperature. Call  $(\Delta L)_1$  the increase when the temperature is raised by  $1^\circ$  K. Then the thermal expansion coefficient is defined by

$$\tau = (\Delta L)_1 / L. \quad (1)$$

This coefficient increases with temperature. However, when we consider simple solids at room temperature, the increase of  $\tau$  is small compared to its value within an interval of, say,  $100^\circ$ . The increase of length  $\Delta L$  is proportional to an increase  $\Delta T$  of temperature:  $\Delta L / L = \tau \Delta T$  as long as  $\Delta L \ll L$ .

In order to estimate roughly the value of  $\tau$ , we assume for a moment that  $\Delta L$  is proportional to  $\Delta T$  even for large changes of  $\Delta L$ . Assume we deliver energy to the rod amounting to the binding energy  $\epsilon_B$  per atom.  $\epsilon_B$  is the energy necessary to liberate an atom from the material. If we did this, the substance would fall apart. Let us now very qualitatively equate "falling apart" with a doubling of the interatomic distances, hence a doubling of the length of the rod  $\Delta L = L$ . Let us further assume that the linear dependence of  $\Delta L$  on  $\Delta T$  more or less holds even up to temperatures corresponding to  $\epsilon_B$  per atom.  $\Delta T$  is a measure of the energy given to an atom. For example, a rise of temperature by  $1^\circ$  corresponds roughly to an energy increase of the order of the Boltzmann constant  $k$  per atom, which is  $\sim 10^{-4}$  eV. (The equipartition theorem ascribes the energy  $3kT$  to a three-dimensional oscillator, so that the energy increase would be  $3k$ . But we are interested only in the vibrations in one direction when we study the linear expansion of the rod.) If the linear dependence of  $\Delta L$  with  $\Delta T$  holds, the increase  $(\Delta L)_1$  for  $\Delta T = 1^\circ$  should be smaller than the increase  $\Delta L = L$  when each atom gets  $\epsilon_B$ , roughly by the ratio  $k/\epsilon_B$ . Therefore, we get

$$\tau = \frac{(\Delta L)_1}{L} \approx \frac{k}{\epsilon_B} \approx \frac{10^{-4}}{(\epsilon_B)_{\text{eV}}}, \quad (2)$$

where  $(\epsilon_B)_{\text{eV}}$  is the binding energy in eV, which is of the order of a few eV for substances that are solid at room temperature.

Table I shows that most expansion coefficients of such solids are indeed of the order of several  $10^{-5}$ . The simple

Table I. Estimated and observed values  $\tau_e$  and  $\tau_{\text{ob}}$  of the thermal expansion coefficient, together with values of the binding energy  $(\epsilon_B)_{\text{eV}}$  and the Debye temperature  $\theta$ . The estimated  $\tau_e$  is taken from (6); the other values are taken from Ref. 1.

Substance	$\tau_e \times 10^5$	$\tau_{\text{ob}} \times 10^5$	$(\epsilon_B)_{\text{eV}}$	$\theta$ (K)
Li	2.7	4.5	1.6	344
Na	3.9	6.9	1.1	158
Al	1.3	2.3	3.4	428
C (diamond)	0.58	0.1	7.4	2230
Fe	1.0	1.2	4.3	470
Ni	1.0	1.3	4.3	450
Si	0.94	0.25	4.6	645
Cu	1.2	1.6	3.5	450
Rb	5.1	9.1	0.85	56
Pb	2.2	2.9	2.0	105

reason is that an increase of  $1^\circ$  corresponds to an increase of energy  $10^{-4}$  to  $10^{-5}$  smaller than the binding energy.

The conclusion resulting in (2) is based upon the assumption that the expansion is proportional to  $\Delta T$ . Let us now show that, for small temperature changes, the expansion is indeed linear in  $\Delta T$ . To get an idea what it is all about, let us look at two neighboring atoms oscillating around their equilibrium positions a distance  $d$  apart. This should symbolize a pair of atoms in the rod, with  $d$  the interatomic distance. The actual distance is  $d + x$ , where  $x$  is the deviation from equilibrium. As long as the potential energy  $V$  is quadratic in  $x$ — $V = ax^2$ —the motion is harmonic and the average of  $x$  is zero, independent of the energy of vibration. Harmonic motion is symmetric about the center and would not lead to an expansion. But we expect an anharmonicity since the restoring force is somewhat reduced for  $x > 0$  and increases for  $x < 0$ . The resistance against stretching decreases at larger distances, and the resistance against shortening increases at smaller distances compared to the harmonic situation. This can be expressed in first order by a cubic term in the potential  $V$ :

$$V = ax^2 - bx^3, \quad a, b > 0. \quad (3)$$

In an oscillatory motion the kinetic energy vanishes at the extreme values  $x_{\pm}$  of  $x$ . Therefore, we equate  $V$  with the total energy at  $x = x_{\pm}$ . The equipartition theorem tells us that the thermal energy of an harmonic oscillator is  $kT$ ; that will still be right if the anharmonic corrections are small. We then get

$$kT = ax_{\pm}^2 - bx_{\pm}^3. \quad (4)$$

For  $b = 0$  we find  $x_{\pm} = \pm (kT/a)^{1/2}$ . At room temperature the cubic term is small compared to the quadratic term, so that we may determine  $x_{\pm}$  for  $b \neq 0$  by putting the  $b = 0$  value into the second term of (4):

$$x_{\pm} = \frac{kT}{a} \left( 1 \pm \frac{b}{a} \sqrt{\frac{kT}{a}} \right),$$

where the square root is to be taken positive. We therefore find  $x_+$  and  $x_-$  by again observing that the second term in the bracket is small compared to unity:

$$x_+ = + \sqrt{\frac{kT}{a}} + \frac{b}{2a} \frac{kT}{a},$$

$$x_- = - \sqrt{\frac{kT}{a}} + \frac{b}{2a} \frac{kT}{a}.$$

The two extreme values are no longer opposite and equal; they are both shifted to larger values by

$$\delta = (b/2a^2) kT. \quad (5)$$

The average  $\bar{x}$  of  $x$  is no longer zero but near  $\delta$ . It may not be exactly equal to  $\delta$  because the anharmonic motion leads to a different averaging but, within our accuracy,  $\bar{x} \approx \delta$ .

We can estimate the values of  $a$  and  $b$  by considering what happens to  $V(x)$  when  $x = d$ . Then, of course, (3) is no longer valid and terms of higher order would become important. We expect  $V(x)$  to be near the binding energy  $\epsilon_B$  for  $x \approx d$ . It is then plausible to assume that the terms of the expansion (3) are of the order of  $\epsilon_B$ . We then may set  $a \sim \epsilon_B/d^2$ ,  $b \sim \epsilon_B/d^3$ , and get from (5) the relative expansion to be  $(\delta/d) \approx \frac{1}{2} (kT/\epsilon_B)$ . We suppose that the length of

the rod increases by the same relative amount as the distance between atoms. The expansion coefficient (1) is the relative expansion per degree and we get

$$\tau \approx \frac{1}{2} \frac{k}{\epsilon_B} = 0.43 \frac{10^{-4}}{(\epsilon_B)_{\text{eV}}}, \quad (6)$$

which is almost the same result as (2) resulting from an even rougher estimate.

Table I compares the observed  $\tau$  at room temperature with the experimental values. It also lists  $(\epsilon_B)_{\text{eV}}$  and the Debye temperatures  $\theta$ . The values from (6) are in reasonable agreement with the facts, considering the rough estimates. Sometimes Eq. (2) would have given better agreement. Diamond and silicon are exceptions. In these cases, however, the Debye temperature is much higher than room temperature. This means that a good part of the atomic

vibrations are not excited, so that our assumption of an energy  $kT$  per linear oscillation is not justified. For diamond,  $\tau$  reaches already 0.51 at 1400 K and for silicon it is 0.45 at 1200 K. As expected, Eq. (6) gives better results at those elevated temperatures.

Victor F. Weisskopf and Herbert Bernstein

<sup>1</sup>*American Institute of Physics Handbook* (AIP, New York, 1972), 3rd. ed.; C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), 5th ed.

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## PROBLEM: TORRICELLI'S NOZZLE

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A cylindrical tank with radius  $R$  is filled with water to a height  $H$ . A hole with radius  $r$  is drilled in the side of the tank and a nozzle with an adjustable angle of elevation is

inserted in the hole. What is the maximum range of the water from the nozzle? (Solution is on page 1182.)

## Search for Simplicity: Maxwell, Rayleigh, and Mt. Everest

Victor F. Weisskopf

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## ADVERTISEMENT





In a paper written in 1899<sup>1</sup> Lord Rayleigh quotes a letter which he received from James C. Maxwell in 1873, who was spending some weeks in Darjeeling, India. I like to imagine Maxwell sitting on the hotel terrace and admiring the view of Mt. Everest, wondering how clearly the mountain was visible at a distance of about 150 km. He wrote, among other things: "I have left your papers on the light of the sky, etc. at Cambridge and it would take me, even if I had them, some time to get them assimilated sufficiently to answer the following question, which I think will involve less expense to the energy of the race if you stick the data into your formula and send me the result... Suppose that there are  $N$  [molecules] per unit of volume of the medium. Find the index of refraction of the compound medium and the coefficient of extinction of light passing through it. The inquiry into scattering must begin by accounting for the great transparency of air..." It is not known what Rayleigh answered. The paper in which he quoted the letter was written 26 years later and was inspired by thinking further about Maxwell's question.

I will take the liberty of inventing a possible answer by Rayleigh to Maxwell in 1873. Let us keep in mind that the electron was unknown at that time. Nobody knew anything about the electric structure of molecules or atoms. It was known, however, that matter can be polarized in an electric field, so that Rayleigh could have written down the formula

$$d = \alpha E, \quad (1)$$

where  $d$  is the strength of the dipole induced in an air molecule by an electric field  $E$ . There are  $N$  molecules per  $\text{cm}^3$ . Therefore the polarization  $P$  of air in the presence of an external field  $E$  is  $P = Nd = N\alpha E$ , a formula which is valid because air is a material of very low density so that we can neglect the polarizing effect of the fields of the neighboring dipole moments. The electric susceptibility  $\chi$  is defined by  $P = \chi E$ , hence  $\chi = N\alpha$ . The connection between  $\chi$  and the dielectric constant was known to be

$$\epsilon = 1 + 4\pi\chi,$$

and so was the relation  $n^2 = \epsilon$  between the index  $n$  of refraction and  $\epsilon$ . Therefore Rayleigh would have written

$$n^2 - 1 = 4\pi N\alpha. \quad (2)$$

What about extinction? When a plane light wave of a given frequency  $\omega$  travels through air, each molecule becomes a vibrating dipole according to (1), where  $E$  is the electric field of the light wave. Rayleigh also knew that a single dipole, vibrating with a frequency  $\omega$ , radiates energy in all directions at the rate of  $s$  ergs/s:

$$s = \frac{2}{3} \frac{\omega^4}{c^3} \overline{d^2} = \frac{2}{3} \frac{\omega^4}{c^3} \alpha^2 \overline{E^2},$$

where a bar over a magnitude means its time average.

We consider air as an ideal gas, so that the location of each air molecule is completely at random. Furthermore, we neglect again the electric effects of the neighboring molecules (this is identical with the condition  $\epsilon - 1 \ll 1$ , which is well fulfilled). Then the radiation of the molecules is completely incoherent and the energy  $S$ , radiated away per second by the molecules in one  $\text{cm}^3$  under the influence of the incident light is

$$S = Ns = \frac{2}{3}(\omega^4/c^3)N\alpha^2 \overline{E^2}. \quad (3)$$

The energy flux (ergs/ $\text{cm}^2/\text{s}$ ) of the light wave is

$$F = (1/4\pi)c \overline{E^2}. \quad (4)$$

The flux decreases along the path of the light parallel to the  $x$  axis because the energy  $S = Ns$  is lost in each  $\text{cm}^3$ , so that we get from (3) and (4)

$$\frac{dF}{dx} = -S = -\frac{8\pi}{3} \frac{\omega^4}{c^4} \alpha^2 NF$$

or  $F = F_0 \exp(-x/L)$ , with

$$L^{-1} = (8\pi/3)(\omega^4/c^4)\alpha^2 N, \quad (5)$$

where  $L$  is the extinction length, the distance in air at which the light intensity is diminished by a factor  $1/e$ .

Now Rayleigh would have compared (5) with (2), and eliminated the then completely unknown quantity  $\alpha$ :

$$L = (3\pi/2)\lambda^4 [N/(n-1)^2]. \quad (6)$$

Here the relations  $n^2 - 1 \approx 2(n-1)$  and  $\lambda = 2\pi c/\omega$  were used. The shorter  $L$ , the stronger the extinction. This formula is the well-known explanation of the blue color of the sky: The extinction and therefore the scattering of sunlight is proportional to  $\lambda^{-4}$ , whereas  $n-1$  is known to depend weakly on  $\lambda$ . It has the value  $0.28 \times 10^{-3}$ .

What about  $N$ ? Avogadro's number was not too well known at that time. Rayleigh probably would have used a value for  $N$  derived by Maxwell of  $1.9 \times 10^{19}$  per  $\text{cm}^3$  for standard conditions, a number quoted in his 1899 paper.<sup>1</sup> The actual number is  $2.7 \times 10^{19}$ . Either number must be reduced by a factor 0.75 for the height of Darjeeling. With his number of  $N$ , he would have gotten 112 km for the extinction length at a wavelength of  $5.8 \times 10^{-5}$  cm. Considering the fact that a light beam from Mt. Everest to Darjeeling goes mostly through air of lower density than that at the endpoint, the result definitely explains that the great mountain was easily visible at Darjeeling. Had he used the correct value of  $N$  he would have arrived at  $L = 160$  km, implying even greater visibility.

Rayleigh was aware that the extinction of light in the atmosphere may also be caused by dust or water vapor. Thus the value (6) is an upper limit. In his 1899 paper he draws attention to the counterintuitive conclusion from (6) that  $L$  is proportional to  $N$ ; if the air is denser it becomes more transparent! He says it in this manner: "If  $N$  be regarded as altogether unknown we may reverse our argument and we then arrive (from the visibility of Mt. Everest) at the conclusion that  $N$  cannot be greatly less than was estimated by Maxwell." A lower number would have given a lower value of  $L$ , a stronger extinction. This seemingly paradoxical state of affairs comes from the fact that  $(n-1)$  is an experimentally fixed number in these discussions. Of course, the value of  $(n-1)$  is proportional to  $N$  [see Eq. (2)], so that  $L$  is indeed inversely proportional to  $N$  as expected.

Let us now jump into the 20th century. Today we can determine the polarizability of a molecule in the air. We can get a rough estimate by replacing the molecule by an oscillator of frequency  $\omega_0$ ; this is the principal resonance frequency of the molecule. Let  $e$  be the electronic charge and  $m$  the mass of the oscillator. The amplitude  $x$  of an

oscillation forced upon it by an electric field  $E$  of frequency  $\omega$  is

$$x = (e/m) [E/\omega_0^2 - \omega^2]. \quad (7)$$

An air molecule has two kinds of resonance frequencies, in the infrared and in the ultraviolet. The former come from the vibrations of the atomic nuclei, the latter from electron vibrations. Because of the mass in the denominator of (7), only the electron vibrations are important. For vibrations produced by visible light,  $\omega^2$  can be neglected compared to the ultraviolet  $\omega_0^2$ . The oscillating dipole is  $d = ex$  and therefore (1) and (7) give

$$\alpha \approx e^2/m\omega_0^2, \quad (8)$$

where  $m$  is the electron mass. It shows that  $\alpha$ , and therefore

$(n - 1)$ , does not depend strongly on the light frequency  $\omega$ , in contrast to the emitted intensity (3). Inserting the known values of  $(n - 1)$  and  $N$  into (4) we obtain a value for  $\alpha$  which, when compared with (8), gives a resonance frequency of  $\omega_0 = 1.25 \times 10^{16}$  corresponding to a wavelength of 1600 Å. Indeed the ultraviolet absorption of air begins at wavelengths of 2000 Å and extends further into the ultraviolet. An average of 1600 Å in Eq. (8), therefore, is quite satisfactory.

Victor F. Weisskopf

<sup>1</sup>Lord Rayleigh, *Philos. Mag.* **47**, 375 (1899).

## PROBLEM: DEPRESSURIZATION OF A SPACECRAFT

One of the fears of space travelers is that a meteor could penetrate the hull of the ship, leading to rapid air loss and depressurization of the cabin.

If a meteor did punch a hole 10 cm<sup>2</sup> in area in the cabin wall, how long do we have to place a steel plate over the

hole before 10%, 30%, and 50% of the air is gone? Assume the volume of the cabin is 100 m<sup>3</sup> and that the air is 50% N<sub>2</sub> and 50% O<sub>2</sub> with initial pressure of 1 atm and initial density 1.25 kg/m<sup>3</sup>. (Solution is on p. 83.)

## Good physics, bad history

Victor Weisskopf

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## LETTERS TO THE EDITOR

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### GOOD PHYSICS, BAD HISTORY

My column, "Search for Simplicity: Maxwell, Rayleigh and Mt. Everest"<sup>1</sup> contains several historical errors which I discovered with the help of John Howard, editor of *Applied Optics*, who is an expert on Lord Rayleigh; and with the help of C. W. F. Everitt, who is an expert on Maxwell. I was misled by the letter from Maxwell to Rayleigh, quoted in Rayleigh's paper,<sup>2</sup> without telling the place of origin, in which Maxwell wondered about the great transparency of air. Later in the same paper, Rayleigh used the example of Mt. Everest appearing "fairly bright at 100 miles distance, as seen from the neighborhood of Darjeeling." Maxwell said in his letter that he "left your [Rayleigh's] papers at Cambridge," from which I concluded that he was on vacation and that the letter came from Darjeeling. This led to my story of Maxwell sitting on the terrace of a hotel admiring the sight of Mt. Everest.

The facts are different: First, Mt. Everest cannot be seen from the hotel in Darjeeling. One must travel several miles to a place where it is visible. Second, Maxwell never was in Darjeeling; the quoted letter most probably was written from Glenlair, in Scotland. But Lord Rayleigh had been in Darjeeling in 1897 and saw Mt. Everest at that time. This may have been an incentive to take up again the question of transparency of air which Maxwell raised in his letter of 1873.

I hasten to add that the physics of my column is correct. It was couched in a historical phantasy.

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<sup>1</sup>V. Weisskopf, *Am. J. Phys.* **54**, 13 (1986).

<sup>2</sup>Lord Rayleigh, *Philos. Mag.* **47**, 375 (1899).

### CHARGE MOMENTUM?

A number of physicists enjoy manipulating the fundamental constants of nature into various combinational groups. In this regard it might be of interest to point out that in the MKSA system of units the value of Planck's constant  $h$  divided by the product of the speed of light  $c$  and elementary unit of charge  $e$  is numerically very close to the value of Boltzmann's constant  $k$ . Using seven significant figures<sup>1</sup> the value of  $h/(ce)$  differs from Boltzmann's constant by less than one part in a thousand, or  $(cek)/h = 1.0008$ . This close agreement leads to an interesting speculation with respect to the units and some interesting possible physical laws. If Boltzmann's constant were equal to the ratio  $h/(ce)$  then the Kelvin temperature unit would have to equal (dimensionally) the product of charge times acceleration. One could then define "charge momentum" as the product of the charge times the velocity and the unbalanced absolute temperature would thus equal the time rate of change of the charge momentum, in analogy with Newton's second law of motion. And, if the unbalanced temperature were zero during a collision process then one would have a conservation law of "charge momentum."

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<sup>1</sup>The values used are  $h = 6.626\,176\,E - 34$  Js,  $c = 2.997\,925\,E + 8$  m/s,  $e = 1.602\,189\,E - 19$  C, and  $k = 1.380\,662\,E - 23$  J/K.

### REDUCED MASS AND THE BOHR RADIUS

In a recent note in this Journal,<sup>1</sup> J. D. McGervey helpfully points out an error which is found in a large number of modern physics discussions. He

makes it clear that this error results from using the reduced mass to calculate the radius of the electron orbit in the Bohr model of the hydrogen-like atom. Rather, it is the mass of the orbiting particle that should be used: Using the reduced mass gives the separation of the two particles in the Bohr model.

The purpose of this letter is to point out that there is another place that this confusion and potential for large error is found. Many modern physics and quantum mechanics texts also make essentially the same error in discussing the radial solutions to the Schrödinger wave equation (SWE) for the hydrogenlike atom. Typically, the radial solutions (and, of course, the complete wavefunctions) contain the parameter  $a_0$ . Most books identify  $a_0$  as "the Bohr radius" or "the radius of the first Bohr orbit."

However,  $a_0$  is *not* the radius of the first Bohr orbit. The SWE and this resulting parameter include the reduced mass, not the mass of the orbiting particle. Therefore,  $a_0$  is actually the separation of the two particles in the ground state of the Bohr model for  $Z = 1$ . For the hydrogen atom itself, the difference between separation and orbit radius is small, but for positronium, muonic atoms, etc., large errors can result from confusing them.<sup>1</sup>

There is no reasonable way for the author of this letter to check every modern physics and quantum mechanics book in print for this confusion. Two texts<sup>2</sup> were found out of the 20 or so checked that did distinguish between the radius and the separation. They did so by using  $a_0$  for the radius and  $a'_0$  for the separation, with  $a'_0$  appearing correctly in the solutions to the SWE.

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## Search for Simplicity: Mountains, waterwaves, and leaky ceilings

Victor F. Weisskopf

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## ADVERTISEMENT



## Search for Simplicity: Mountains, waterwaves, and leaky ceilings

We would like to find a reason why the highest elevations of mountains on Earth are of the order of 10 km. It must be connected with the rigidity of rock. We assume that the volcanic and tectonic activity of the Earth produces elevations and depressions of the Earth's surface. What limits the height of the elevations? We simplify a mountain by a block of silicon oxide resting on a plane surface of the same material (see Fig. 1). The mountain will be too high to be supported by the base when the block is so large that the base matter starts to flow; the mountain will have reached its maximum height when plastic deformation sets in.

Let  $H$  be the height of our block at which it begins to sink. The  $H$  will be roughly the maximum height which a mountain can reach. This height is reached when the energy gained by letting the mountain sink is equal to the energy necessary to engender plastic flow. The amount of matter undergoing plastic deformation is about equal to the amount of mountain matter which sinks into the ground. The sinking of the mountain by the amount  $\delta \ll H$  is equivalent to moving a layer of thickness  $\delta$  from the top into the ground, displacing a comparable volume by plastic flow. Hence, roughly speaking, the amount of gravitational energy gained by lowering matter from the height  $H$  to the ground must be equal to the energy for plastic deformation of the same amount of matter. The calculation can be done for each molecule separately. Let us call  $\epsilon_p$  the energy per molecule necessary to induce plastic flow. Then we get the relation

$$AmHg = \epsilon_p, \quad (1)$$

where  $A = 60$  is the molecular weight of  $\text{SiO}_2$ ,  $m$  is the mass of a proton, and  $g$  is the gravitational acceleration on Earth.

How can we get an estimate of  $\epsilon_p$ ? Plastic flow is a rearrangement of the molecules. When it occurs the molecules must pass through spatial arrangements that would not occur in the solid phase but rather in the liquid state. We get an idea of the energy necessary to get to these states by melting the substance and then supercooling the liquid back to the original temperature. Assuming that the heat capacities of the solid and the supercooled liquid state are the same, the energy necessary for this process is the melting heat  $\epsilon_M$  at melting temperature. For  $\text{SiO}_2$   $\epsilon_M = 0.148$  eV per molecule. We therefore conclude that  $\epsilon_p \approx 0.15$  eV. We then obtain  $H \approx 14$  km. This result is surprisingly close to the actual value of 10 km.

This estimate is based upon a competition between two effects: the gravitational force and the rigidity of the mate-

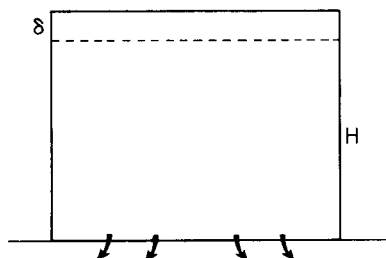


Fig. 1. The sinking of the mountain by the amount  $\delta$  corresponds to the displacement of a layer of thickness  $\delta$  from the top into the ground, and to a plastic flow of a comparable volume in the ground.

rial. The energy  $\epsilon_p$  measuring the rigidity is connected with atomic energies. It is a fraction  $\xi \epsilon_B$  of the binding energy  $\epsilon_B = 6.5$  eV (the energy needed to extract a molecule from solid  $\text{SO}_2$ ). As expected, the coefficient  $\xi$  is rather small:  $\xi = 0.023$ . The binding energy  $\epsilon_B = \eta \text{ Ry}$  is of the order, but smaller, than the Rydberg energy  $\text{Ry} = me^4/2\hbar^2$ , with  $\eta = 0.48$ . Expressed in fundamental constants, we get

$$H = \xi \eta \text{ Ry} / (Amg). \quad (2)$$

Let us now look at two other seemingly very different natural phenomena: the size of drops on a leaky ceiling, and water waves on the surface of a lake. What is the size of the drops forming on a leaky ceiling when they fall down? The leaking water forms a thin film on the surface which is unstable. A slight accumulation at one point starts growing downwards by water flowing into it from all sides, since this reduces the gravitational energy (see Fig. 2). When will the drop come off?—when the gravity force becomes larger than the surface tension that keeps the drop on the ceiling. The surface tension  $S$  is an energy per unit area or a force per unit length. Let us approximate the drop as a hemisphere of a radius  $R$  pointing downwards. Then the force  $F$  holding it up is the surface tension along the periphery where the drop merges with the film on the surface:  $F = 2\pi RS$ . When this force becomes equal to the gravity force  $(2\pi/3)R^3\rho g$ , the drop will fall. Here,  $\rho$  is the density of water. We then get for the radius of the drop ( $S = 73$  dyn/cm in water):

$$R \approx (3S/g\rho)^{1/2} = 0.47 \text{ cm}. \quad (3)$$

The result is not exact since the form of the drop when attached to the ceiling deviates from a hemisphere, in particular shortly before separation. However, it does give a size of the drops not far from the one we do observe all too frequently.

Let us now turn to the water waves. When a light breeze starts blowing over a quiet surface of a lake, the wavelength  $\lambda$  of the initial waves is of the order of a few centimeters. "Willows whiten, aspens quiver, little breezes dusk and shiver" as the poet Tennyson says. We will not enter into the physics of wave production; suffice it to say that the wind transfers its energy first to those waves whose propagation velocity  $v$  is lowest. The expression for  $v$  is

$$v = (g\lambda + S/\lambda\rho)^{1/2},$$

where  $S$  is the surface tension,  $\rho$  the density of water, and  $\lambda = \lambda/2\pi$ . The first term comes from the gravity and the second term from the surface tension. It is evident that the longer  $\lambda$ , the stronger gravity acts as a restoring force, and the smaller  $\lambda$  the more the curvature of the surface causes a restoring force. The minimum of  $v$  occurs at

$$\lambda_m = (S/g\rho)^{1/2} = 0.28 \text{ cm}. \quad (4)$$

The corresponding minimum value  $v_m$  is 23 cm/s. A wind with less than this speed would be unable to produce waves.

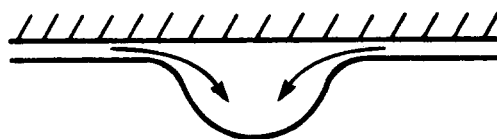


Fig. 2. The forming of a water drop from a thin water film below a surface.



This is why lakes are so much like mirrors, even in the presence of weak winds. The first waves appear when the breeze surpasses  $v_m$ , and should have a wavelength of  $2\pi\lambda_m$ . Actually the minimum velocity  $v_m$  is somewhat smaller and the corresponding wavelength  $\lambda_m$  is somewhat larger, because we should have done our estimate by using the group velocity instead of the phase velocity of the waves, but the order of magnitude is the same. We would have found  $v_m = 18$  cm/s, and  $\lambda_m = 4.4$  cm. Note that  $\lambda_m$  is the same length as the radius of the falling drop as given by (3) apart from a factor  $\sqrt{3}$  for the phase velocity calculation or a factor 0.68 for the group velocity calculation.

In order to compare these results with the mountain height, we express  $S$  and  $\rho$  in terms of molecular properties. The binding of a molecule at the surface is  $(1 - \xi')$  times the binding energy  $\epsilon_B$  in the interior. In the January 1985 installment,<sup>1</sup> we found that  $\xi'$  is about  $\frac{1}{2}$ . In water it is somewhat smaller:  $\xi = 0.093$ . The surface tension expressed as energy per unit surface is  $S = \xi'\gamma' \text{ Ry} \cdot d^{-2}$ , where  $\epsilon_B = \gamma' \text{ Ry}$  and  $d$  is the distance between molecules so that  $d^{-2}$  is the number per  $\text{cm}^2$  of surface. For water,  $\gamma' = 0.037$ , and the density is  $\rho = A'm/d^3$ ; where  $A'$  is the molecular weight of water  $A' = 18$ . We then get

$$\lambda_m^2 = \frac{R^2}{3} = \frac{\xi'\gamma' \text{ Ry}}{gA'm} d = C \cdot d \cdot H, \quad C = \frac{\eta'\eta'A}{\eta\eta'A'},$$

where the second equality comes from a comparison with (2). The factor  $C$  is not too far from unity:  $C = 1.8$ . In other words,  $\lambda_m$  and the size of falling drops  $R$  are roughly the geometric mean between the maximum height of the mountains and the intermolecular distance  $d$ .

How about the maximum height of mountains on other planets? For this aim we must express the earthbound quantity  $g$  by means of Newton's constant  $G$ :  $g = GM/R_p^2$ , where  $M$  and  $R_p$  are the mass and radius of the Earth. We put  $M = (4\pi/3)R_p^3\rho_p$ , where  $\rho_p = 5.5 \text{ g/cm}^3$  is the mean density of the planet. We then get the value  $g = (4\pi/3)G\rho_p R_p$ , and from (2):

$$H = R_0^2/R_p, \quad R_0^2 = (3/4\pi)\xi\eta \text{ Ry}/(AmG\rho_p). \quad (5)$$

With the values of  $\xi$ ,  $\eta$ , and  $\rho$  valid for the Earth, the length  $R_0$  is 300 km. Equation (5) tells us that the maximum elevations on different planets are inversely proportional to the radius if the material properties are nearly the same, as they are more or less for Mars and our moon. Thus the mountains and valleys on Mars ought to be about twice as high or deep than on Earth. This is indeed the case. The elevations on the moon ought to be six times larger; actually they are much lower. This is because, in contrast to the Earth and Mars, the moon has had no tectonic activity for a

long time, so that its surface has been flattened by meteoric erosion and other causes.

According to (5), a celestial body of a radius  $R \lesssim R_0$  would sustain mountains comparable to its radius. Such a body could be nonspherical if no liquefaction took place after it assumed such a shape. The gravity would be no longer able to produce an approximate sphere by plastic deformation. The critical radius is  $R \sim 300$  km if the material composition is similar to that of the Earth. Indeed all known nonspherical celestial bodies, such as the moons of Mars and some moons of Saturn, are smaller than  $R_0$ .

It is instructive to express  $H$  or  $\lambda_m$  not in an anthropomorphic unit such as kilometer but in terms of the only "dignified" unit among atoms: the Bohr-radius  $a = \hbar^2/(me^2) = 0.53 \times 10^{-8}$  cm. Also, let us get rid of all nonatomic quantities in expression (5) such as the density  $\rho_p$  and the radius  $R_p$  of the planet, and express them in terms of  $N_p$ , the number of nucleons (protons and neutrons) in the planet. Fortunately, the main constituents  $\text{SiO}_2$  and Fe have a very similar molecular weight, say,  $A \sim 60$ . We introduce a distance  $d$  between them, which is defined by  $(N_p/A)d^3 = (4\pi/3)R_p^3$ , and express it as a multiple of the Bohr radius:  $d = fa$ , where  $f$  turns out to be 4.9 for the Earth. We then get altogether for the maximum height of mountains in terms of the Bohr radius

$$\frac{H}{a} = 0.19\xi\eta f^2 \frac{\alpha}{\alpha_g} \frac{1}{A^{5/3}N_p^{1/3}} = 2.6 \times 10^{14}. \quad (6)$$

Here  $\alpha/\alpha_g$  stands for  $e^2/GM^2$ , whereby  $\alpha = e^2/\hbar c = (137)^{-1}$  and  $\alpha_g = GM^2/\hbar c = 6.1 \times 10^{-39}$ . The former is the electromagnetic fine structure constant, the latter is its analog for gravity. The appearance of the ratio of these constants is an indication that  $H$  is the result of a competition between the atomic forces which are electric effect governed by quantum mechanics, and gravity effects. The smallness of  $\alpha_g$  is compensated by the large number  $N_p^{1/3}$ . The square root of (6) gives the wavelength  $\lambda_m$  produced by a breeze on a lake, and the radius of a falling drop, in terms of the Bohr-radius. Adjusting the constants  $\xi$ ,  $\gamma$ ,  $f$ , and  $A$  to water, we get  $\lambda_m/a \approx 10^7$ . The greatness of mountains, the finger sized drop, the shiver of a lake, and the smallness of an atom are all related by simple laws of nature.

Victor F. Weisskopf

<sup>1</sup>Am. J. Phys. 53, 19 (1985).

## Physics of mountains—response

Victor F. Weisskopf

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### CORNU'S SPIRAL AND THE MICROCOMPUTER

M. B. Stewart's reworking<sup>1</sup> of Hastings' rational approximation for the Fresnel integrals is given in the standard handbook by Abramowitz and Stegun,<sup>2</sup> formulas 7.3.9–10 and 7.3.32–33 (pp. 301–302), and in many other references.

Improved precision, both for the Hastings formulas and for higher-order approximations, is available in a recent paper.<sup>3</sup>

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11 March 1986

<sup>1</sup>M. B. Stewart, *Am. J. Phys.* **54**, 280 (1986).

<sup>2</sup>M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1965).

<sup>3</sup>M. A. Heald, *Math. Comp.* **44**, 459 (1985). There is a typographical error in Eq. (3); the positive sign between the two terms should be negative.

### ON CALCULATING FRESNEL INTEGRALS

I read with interest the article by Stewart<sup>1</sup> on calculating Fresnel integrals with a precision of about three decimal places by using a microcomputer. I have developed a program in BASIC which may be of use to some readers. It calculates Fresnel integrals accurate to six decimal places for all positive values of  $v$ . When applied to optical diffraction, the parameter  $v$  is defined in terms of the phase difference at a detector between signals from different strips of an aperture:  $(\pi/2)v^2 = \text{phase difference}$ . For  $v < 1.9$  the program uses the first eleven terms of the power series derived by integrating the standard expansions of the sine and cosine functions. For  $v > 1.9$  it takes advantage of the fact

that the Cornu spiral is centered at  $(0.5, 0.5)$  with radius approximately  $1/\pi v$  and polar angle approximately  $\pi(v^2 - 1)/2$ . The difference between this approximation and the true Cornu spiral was empirically fit to a five-term power series in  $1/v^2$ . The "actual" power series in  $1/v^4$  is divergent. This program is much longer than the one which can be written using Stewart's formulas, but the time required for execution, once the coefficients are set, is about the same ( $\frac{1}{8}$  s). For  $v > 1.9$  the majority of time is spent by my microcomputer (TI professional) in computing the trigonometric functions. This also consumes most of the time in evaluating Stewart's formulas. It takes about the same time to evaluate the eleven terms of the power series for  $v < 1.9$ .

I will supply the program upon request.

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14 April 1986

<sup>1</sup>M. B. Stewart, *Am. J. Phys.* **54**, 280 (1986).

### PHYSICS OF MOUNTAINS

The article by Weisskopf<sup>1</sup> demonstrated an interesting method for calculating the maximum height of a mountain. However, actual mountains are shaped more like cones or pyramids than right prisms, as Weisskopf assumes. Assume the weight of the mountain is evenly distributed across the base. Then, since the volume of a cone or pyramid is  $\frac{1}{3}AH$  ( $A$  the base area,  $H$  the height), it follows that a mountain with the same mass, density, and base area as Weisskopf's rectangular mountain would have a peak three times as high. This moun-

tain would have the same stress on the base, and so the maximum possible mountain height is 42 km, not 14. (Interestingly, this result is independent of the base width of the mountain.)

The closeness of Weisskopf's result to actual mountain heights is purely coincidental.

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<sup>1</sup>V. F. Weisskopf, *Am. J. Phys.* **54**, 2 (1986).

### PHYSICS OF MOUNTAINS—RESPONSE

The letter by Mr. Landis points out correctly the danger of taking simple semiquantitative results too literally. All one should expect is the right order of magnitude. Even a predicted maximum height of a mountain of 42 km would be a significant result. More over, my estimates were upper limits, also because I have used the melting heat  $\epsilon_M$  as a measure of the energy  $\epsilon_P$  necessary to induce plastic flow. This was done to simplify the argument. But  $\epsilon_P$  is probably only a fraction of the melting heat:  $\epsilon_P = f\epsilon_M$ . Lattice imperfections, cracks, and dislocations reduce the resistance against deformations. A factor  $f \sim \frac{1}{3}$  would take care of most of the objections by Mr. Landis.

Furthermore most of the mountains are created by tectonic upheavals, such as the collision of the Indian subcontinent with the Asian shelf. At the beginning the shapes of the mountains may very well have been nearer to a rectangular prism than to a cone. The latter shape is the effect of erosion. This does not hold, of course, for

mountains formed by volcano activity. But there is no reason why such mountains would reach the maximum height.

Incidentally I would like to correct a misprint in that column. The melting heat  $\epsilon_M = 0.089$  and not 0.148 eV. However the estimate of the height of the mountain was made with the correct value. There is also some confusion in the notation in the first formula on p. 111, but the final values are correct.

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# NOTE ON "THE AXIOMS UNDERLYING MAXWELL'S ELECTROMAGNETIC EQUATIONS" [G. B. WALKER, AM. J. PHYS. 53, 1169 (1985)]

The passage of over 35 years since the appearance of our "Note on the Presentation of Maxwell's Equations" in this very Journal<sup>1</sup> makes it understandable that Professor G. B. Walker might have overlooked our work in preparing his insightful article. We had discussed how certain combinations of

$$\text{Gauss's law } \nabla \cdot \epsilon_0 \mathbf{E} = \rho, \quad (1)$$

$$\text{Ampere's law } \nabla \times \mathbf{H} = \mathbf{J}, \quad (2)$$

Conservation of charge

$$\nabla \cdot \mathbf{J} + \dot{\rho} = 0, \quad (3)$$

Maxwell's 2nd equation without charges

$$\nabla \times \mathbf{H} = \epsilon_0 \ddot{\mathbf{E}}, \quad (4)$$

Maxwell's 2nd equation with charges

$$\nabla \times \mathbf{H} = \epsilon_0 \ddot{\mathbf{E}} + \mathbf{J}, \quad (5)$$

imply the remaining equations. In particular we demonstrated how the combination (1), (3), and (4) leads to (5), and thence trivially to (2). We paid particular attention to accommodating the singularities engendered by the passage of point charges through surfaces of integration. Professor Walker does essentially the same thing, with perhaps less worry about the singularities. We share with Professor Walker the value of the insight afforded by seeing how displacement current implies the magnetic field associated with a current. In fact, we wrote

"...It appears to us that a more suitable method of correlating the concepts (of conduction current and dis-

placement current) is to begin with the displacement current as fundamental, and then proceed to interpret conduction current as a phenomenon of the same nature, magnetically, as the motion of the electric fields surrounding the moving charged particles that constitute the conduction current."

But as much as this view appeals to us, we are not so confident as to which laws should be considered "facts," "doctrines," "axioms," or whatever. That, however, is another story.

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<sup>1</sup>John P. Vinti and D. J. X. Montgomery, Am. J. Phys. 17, 298 (1949).

# REPLY TO THE NOTE BY VINTI AND MONTGOMERY

At first sight it may appear that the two papers cover the same ground and differ only in detail in the calculation of the magnetic effect of a current of point charges. In fact, the subject of Maxwell's equations is approached in very different ways.

The objective of the Walker paper is to examine the following question. Assuming Maxwell's equations to be correct in a particular inertial reference frame (as defined by Einstein) what in fact are the laws of nature underlying these equations? The objective of the paper by Vinti and Montgomery, as stated on p. 299, is to show how one of Maxwell's equations can be derived from a form of that equation (omitting the term indicating electric current density) by the explicit use of an equation expressing conservation of charge. In other words, they are concerned primarily with a mathematical issue and in their current note quite properly refer to the Walker paper as "another story."

It is to be hoped that the two papers will stimulate interest in basic questions in electromagnetism which for many years have come to be regarded as dead issues by teachers, writers, and journal review boards. That flaws in

Maxwell's arguments have been exposed is surely reason for teachers to be wary of repeating these same arguments solely on the grounds of tradition. My only criticism of the excellent paper by Vinti and Montgomery is that they continue to speak of "displacement current" a phrase Maxwell himself might now regret having introduced.

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# ON MAXWELL'S FAITH

Paul Theerman's recent article<sup>1</sup> neglected two interesting points regarding James Clerk Maxwell's faith. As Korg<sup>2</sup> has pointed out, the Victorians, among their many phobias, had a tendency to express a kind of "theological agoraphobia," if you will, after learning that the Earth was a minute speck lost in the immensity of the universe. Tennyson, who wrote *In Memoriam, A.H.*—the credo which sums up the nineteenth century crisis of faith—called these vast reaches "the waste places of the sky" (Canto 3). Perhaps Maxwell envisioned future generations cured of this despair by the good news to be discovered in his electromagnetic theory. Because the luminiferous aether "fills the smallest portion" of this immensity, Maxwell believed he had not only unified electricity and magnetism, but had bound the great universe together in unity, as well. Here he seems to be addressing Tennyson.

The vast interplanetary and interstellar reaches will no longer be regarded as waste places in the universe, which the Creator had not seen fit to fill with the symbols of the manifold order of his kingdom.<sup>3</sup>

As for F. D. Maurice, Theerman did not describe the radical implications of his theology, which had him briskly trounced from King's College. In brief, Maurice seemed to interpret the famous phrase, "The kingdom of God is at hand," to mean, "The kingdom of God is at hand, at your very fingertips—in this life, not necessarily in some afterlife. Pick it up and grasp onto it." For his damage to the promise of afterlife, Maurice was regarded as dangerous; as poison.

The interesting question that remains is not so much why Maxwell embraced this enlightened view and