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DIATOMIC MOLECULES ACCORDING TO THE WAVE MECHANICS I: ELECTRONIC LEVELS OF THE HYDROGEN MOLECULAR ION

By Philip M. Morse and E. C. G. Stueckelberg

Abstract

The electronic energies $W_\rho(n_y, n_\phi, n_x)$ of the hydrogen molecular ion are calculated by means of the wave mechanics as functions of the nuclear separation $c=2\rho$, for several values of the quantum numbers n_y, n_ϕ and n_x. The wave function is separable in the elliptical coordinates $y=(r_1+r_2)/2\rho$, ϕ and $x=(r_1-r_2)/2\rho$. A qualitative idea of the behavior of these energies as ρ changes from infinity to zero is gotten by an investigation of the behavior of the nodal surfaces. The number of these surfaces in any coordinate equals the quantum number in that coordinate. When $\rho=\infty$ the resulting system is that of a hydrogen atom and a separated nucleus, the nodes are paraboloids and planes with quantum numbers n_η, n_ϕ and n_ξ, and the electronic energy is $W_\infty=R/(n_\eta+n_\phi+n_\xi+1)^2$ where R is the lowest energy of the hydrogen atom. When $\rho=0$ the system is that of a helium ion, the nodes are spherically symmetric with quantum numbers n_r, n_ϕ and n_θ, and the electronic energy is $W_0=4R/(n_r+n_\phi+n_\theta+1)^2$. As ρ changes from zero to infinity it is shown that the quantum numbers are related in the manner $n_r\rightarrow n_y\rightarrow n_\eta$; $n_\phi\rightarrow n_\phi\rightarrow n_\phi$; $n_\theta\rightarrow n_x\rightarrow 2n_\xi$ or $2n_\xi+1$. Therefore $W_0=4R/n_\eta+n_\phi+2n_\xi+1)^2$ or $=4R/(n_\eta+n_\phi+2n_\xi+2)^2$. By this rule it is possible to check the following quantitative calculations. The first order perturbations of the various electronic energies of the first three degenerate levels of the helium ion resulting when $\rho=0$ were calculated; the perturbation being the slight separation of the nuclei ($\rho>0$). The first order perturbations of the various electronic energies of the first two degenerate levels of the hydrogen atom resulting when $\rho=\infty$ were calculated when the perturbation was the diminution of the separation ($\rho<\infty$). The first method is not valid for $\rho>a/2$, where a is the radius of the first Bohr orbit of the hydrogen atom, and the second is not valid for $\rho<3a/2$. The gap between was extrapolated by means of the nodal reasoning above. These electronic energies plus the energy of nuclear repulsion give the molecular potential energies. A calculation of these shows that of the eight curves obtained only three, the $1s\sigma$, $3d\sigma$ and $4f\sigma$ states show minima, and therefore are stable configurations to this order of approximation (the Hund molecular notation is used for the states). The numerical results check with previous calculations and with the data available.

Introduction

In THE study of the diatomic molecule one of the most important of its properties is the so-called potential energy curve of the nuclei, giving the energy of the electrons plus the energy of repulsion of the nuclei as a function of the nuclear separation. The simplest case, that of two similar nuclei with a single electron in common (represented by the hydrogen molecular ion) must be investigated first, in order that a general idea of the behavior of one electron be obtained before attacking the problem of the more complicated molecule formed by the addition of more electrons.[1–8]

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[1] For a general qualitative statement of the problem see the papers of Hund and Mulliken.

[2] F. Hund, Zeits. f. Physik **36**, 657 (1926).

It has been shown that the electronic energy (the sum of the electronic potential and kinetic energies) of a diatomic molecule is approximately independent of the rotatory or vibrational velocity of the nuclei, and only dependent on their instantaneous relative separation.[9]

This means that for purposes of calculating this energy the nuclei can be considered as fixed in space at a distance $d=2\rho$ apart. The equation for the wave function of the electron then becomes

$$\nabla^2\Psi+\frac{8\pi^2\mu}{h^2}\left(W_\rho+\frac{e^2Z}{r_1}+\frac{e^2Z}{r_2}\right)\Psi=0$$

where r_1 is the distance from the point in question to the first nucleus and r_2 the distance from the second nucleus. This equation can be separated in elliptical coordinates, $y=(r_1+r_2)/2\rho$, $x=(r_1-r_2)/2\rho$ and ϕ the angle about the nuclear axis.

This means that $\Psi=N\cdot\Phi(\phi)\cdot Y(y)\cdot X(x)$, where N is the normalizing factor. The factor Φ is $e^{im\phi}$, since angle ϕ is a cyclic coordinate, and the equations for the other two factors become

$$\frac{d}{dy}\left[(y^2-1)\frac{dY}{dy}\right]-\frac{m^2Y}{y^2-1}+\frac{8\pi^2\mu\rho^2}{h^2}\left(W_\rho y^2+\frac{2Ze^2}{\rho}y+C\right)Y=0 \tag{1}$$

$$\frac{d}{dx}\left[(1-x^2)\frac{dX}{dx}\right]-\frac{m^2X}{1-x^2}+\frac{8\pi^2\mu\rho^2}{h^2}(-W_\rho x^2-C)X=0. \tag{2}$$

The problem presented by these two equations, namely that of finding values of W and C for which X is finite over the range $-1\leqq x\leqq +1$ and Y finite over the range $+1\leqq y\leqq\infty$, has not been solved in general. Burrau[10] found W_ρ as a function of ρ for the lowest allowed level by a numerical integration which is only applicable to this lowest state.

It is possible to determine what form Ψ takes for the two limiting values of ρ, zero and infinity. When $\rho=0$, Ψ is the wave function of the singly ionized helium atom (the united atom)

$$\Psi_0(n,l,m)=N_0(nlm)\cdot e^{im\phi}\cdot\sin^m\theta\cdot P_l{}^m(\cos\theta)\cdot e^{-r/na_0}\cdot(2r/na_0)^l\cdot L_{n+l}^{2l+1}(2r/na_0) \tag{3}$$

These quantum numbers bear relation to $n_\phi n_r$ and n the quantum numbers for each coordinate, for $n_\phi=m$, $n_\theta=l-m$, $n=n_r+n_\phi+n_\theta+1$. The relation between the spherical coordinates used above and the general ellip-

[3] F. Hund, Zeits. f. Physik **40,** 742 (1927).

[4] F. Hund, Zeits. f. Physik **42,** 93 (1927).

[5] F. Hund, Zeits. f. Physik **43,** 805 (1927).

[6] F. Hund, Zeits. f. Physik **51,** 759 (1928).

[7] R. S. Mulliken, Phys. Rev. **32,** 186 (1928).

[8] R. S. Mulliken, Phys. Rev. **32,** 761 (1928).

[9] Born and Oppenheimer, Ann. d. Physik **84,** 457 (1927).

[10] Burrau, Kgl. Danske Vid. Selskab. **VII,** 14, (1927).

tical coordinates is that as $\rho\rightarrow 0$, $y\rightarrow r/\rho$, $x\rightarrow\cos\theta$ and ϕ remains ϕ. $P_b{}^a$ is the generalized Legendre polynomial; $P_b{}^a(x)=d^aP_b(x)/dx^a$. $L_b{}^a$ is the generalized Laguerre polynomial; $L_b{}^a(x)=d^aL_b(x)/dx^a$.[11] The constant $a_0=h^2/(8\pi^2\mu e^2Z_0)=a/2Z_0$, where a is the radius of the first Bohr orbit in hydrogen ($a=5.4\times 10^{-9}$ cm). The normalizing factor is

$$N(nlm)=\left(\left(\frac{2}{na_0}\right)^3\cdot\frac{1}{2\pi}\cdot\frac{2l+1}{2}\cdot\frac{(l-m)!}{(l+m)!}\cdot\frac{(n-l-1)!}{2n[(n+l-1)!]^3}\right)^{1/2}.$$

For the hydrogen molecular ion the value of Z_0 will be two, and the allowed energy levels for $\rho=0$ are

$$W_0(n)=-2\pi^2\mu Z_0{}^2e^4/n^2h^2=4R/n^2$$

where R is the energy of the normal state of the hydrogen atom.

When $\rho=\infty$ the wave function must represent a hydrogen nucleus infinitely separated from a neutral hydrogen atom (the separated atom) and must represent the fact that the electron is as likely to be about nucleus number one as about nucleus number two. If ψ_1 be the wave function for a single separate hydrogen atom at the position of nucleus one, and ψ_2 the same at nucleus two, then the function which must be used in this limiting case is

$$\Psi_\infty=(\psi_1\pm\psi_2)/(2)^{1/2} \tag{4}$$

the possibility of either sign being due to the fact that $\Psi\,\overline{\Psi}$ and not Ψ, has physical reality, and for $\rho=\infty$ this change in sign makes no change in the value of $\Psi\overline{\Psi}$. Unsöld[12] made the mistake of considering the wave function as entirely about one nucleus when he attacked the problem.

The elliptical coordinates for the general problem become parabolic coordinates $\xi_1=r_1(1+\cos\theta_1)$; $\eta_1=r_1(1-\cos\theta_1)$ about nucleus one, and $\xi_2=r_2(1-\cos\theta_2)$; $\eta_2=r_2(1+\cos\theta_2)$ about nucleus two, with angle ϕ in both cases. In other words, when $\rho\rightarrow\infty$ then $y\rightarrow 1+\eta_1/2\rho$ and $y\rightarrow 1+\eta_2/2\rho$; $x\rightarrow-(1-\xi_1/2\rho)$ and $x\rightarrow 1-\xi_2/2\rho$.

The wave function of the hydrogen atom in parabolic coordinates for the electron about nucleus one is

$$\psi_1=N_\infty e^{im\phi}\left(\frac{\xi_1\eta_1}{n^2a_\infty^2}\right)^{m/2}\cdot e^{-(\xi_1+\eta_1)/2na_\infty}\cdot L_{k+m}^{m}\left(\frac{\xi_1}{na_\infty}\right)\cdot L_{n-k-1}^{m}\left(\frac{\eta_1}{na_\infty}\right) \tag{5}$$

and similarly for ψ_2. Here $a_\infty=a/2Z_\infty$, Z_∞ has half the value of Z_0 for the united atom, and of the quantum numbers $m=n_\phi$, $k=n_\xi$, but otherwise the definitions of the terms are the same. The total quantum number $n=n_\eta+n_\phi+n_\xi+1$ and the normalizing factor

$$N_\infty(nkm)=\left(\frac{4}{2\pi}\,\frac{1}{(na_\infty)^3}\,\frac{2n[(k+m)!]^3[(n-k-1)!]^3}{k!(n-k-m-1)!}\right)^{1/2}$$

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[11] For definitions of P_b and L_b see Courant-Hilbert, (Methoden der Mathematischen Physik, Berlin, 1924.) pp. 67 and 77.

[12] A. Unsöld, Zeits. f. Physik **43**, 563 (1927).

and the allowed energy levels are those of the hydrogen atom

$$W_\infty(n\ k\ m) = R/n^2.$$

Therefore the wave function for the hydrogen molecular ion for infinite separation of the nuclei is, when the parabolic coordinates are transformed to elliptical coordinates,

$$\begin{aligned}\Psi_\infty = \frac{N_\infty}{\sqrt{2}} e^{im\phi} \cdot \left[\frac{2\rho(y-1)}{na_\infty}\right]^{m/2} \cdot e^{-\rho y/na_\infty} \cdot L^m_{n-k-1}\left[\frac{2\rho(y-1)}{na_\infty}\right] \cdot \\ \cdot \left\{\left[\frac{2\rho(1+x)}{na_\infty}\right]^{m/2} \cdot e^{-\rho x/na_\infty} \cdot L^m_{k+m}\left[\frac{2\rho(1+x)}{na_\infty}\right]\right. \\ \left. \pm \left[\frac{2\rho(1-x)}{na_\infty}\right]^{m/2} \cdot e^{+\rho x/na_\infty} \cdot L^m_{k+m}\left[\frac{2\rho(1-x)}{na_\infty}\right]\right\}\end{aligned} \tag{6}$$

according to Eq. (4).

Thus the form of the wave function and the value of the energy levels are known for the two limits of ρ. Presumably the wave functions and energy levels will change continuously from one form to the other as ρ changes from ∞ to 0. The curves obtained for the energy levels will represent the electronic energies and, by adding the repulsion energy $Z^2e^2/2\rho$, the potential energy curves will be obtained.

THE OSCILLATORY PROPERTIES OF Ψ

It is possible to tell qualitatively where these electronic energy curves go (i.e., which states $W_0(n_r n_\phi n_\theta)$ are connected to the states $W_\infty(n_\eta n_\phi n_\xi)$ by continuous curves) by a study of the oscillatory properties of the wave function Ψ for any separation.

It has been shown above that

$$\Psi = N \cdot \Phi(\phi) \cdot Y(y,\rho) \cdot X(x,\rho)$$

where the function $\Phi(\phi)$ is always $e^{im\phi}$ no matter what the value of ρ. The surfaces $Y=0$, $X=0$ and (real part of Φ) $=0$ are called nodal surfaces, and are coordinate surfaces with either ϕ, y or x constant, where Ψ is zero or pure imaginary. As ρ is varied these surfaces change in shape and position but can never change in number, due to the inherent character of the Schroedinger equation.[13] The number of nodes in any coordinate at a finite distance from the nucleus corresponds to the quantum number in that coordinate, and in the case considered the total number of nodes plus one equals the total quantum number n. The meaning of these quantum numbers in terms of a molecular model has been discussed by Mulliken.[7]

The quantum number n_ϕ represents the number of nodal surfaces in ϕ. The number of nodal surfaces in y is called n_y; when $\rho=0$ this becomes n_r, and when $\rho=\infty$ it is n_η. The number of nodal surfaces in x equals n_x, and

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[13] One of us (P. M. M.) will shortly publish a paper dealing with the general properties of these nodal surfaces, and a proof of the above propositions will be included.

when $\rho=0$ it becomes n_θ. The nodes in ϕ are planes in which lies the nuclear axis, and those in y are ellipsoids with the nuclei as foci. The nodes in x are hyperboloids with the nuclei as foci, and as the nuclear separation increases these last surfaces separate out; if n_x is an even number half of them stay about one nucleus and half about the other and $n_x=2n_\xi$; but if n_x is odd one surface stays midway between the nuclei and when $\rho=\infty$ it is an infinite distance from either nucleus, so that $n_x-1=2n_\xi$. No more than one nodal surface can be an infinite distance from either nucleus, for in this space midway between them the potential energy is greater than W and from the nature of the Schroedinger equation, only one nodal surface can be present in such a region.

Therefore it can be seen that for $\rho=\infty$ a hydrogen atom having the quantum numbers n_η, n_ϕ, and n_ξ and having the energy $W_\infty(n_\eta n_\phi n_\xi)=R/(n_\eta+n_\phi+n_\xi+1)^2$, plus a nucleus, will become a molecule having quantum numbers $n_y=n_\eta$; $n_\phi=n_\phi$ and $n_x=2n_\xi$ or $=2n_\xi+1$ according as there is or is not a nodal plane midway between the nuclei. This molecule will, when $\rho=0$, become a united atom with quantum numbers $n_r=n_\eta$; $n_\phi=n_\phi$ and $n_\theta=2n_\xi$ or $=2n_\xi+1$, having the energy

$$W_0(n_r n_\phi n_\theta)=4R/(n_\eta+n_\phi+2n_\xi+1)^2$$

or

$$=4R/(n_\eta+n_\phi+2n_\xi+2)^2.$$

As ρ changes from infinity to zero W_ρ changes from the above set of values of W_∞ to the corresponding set of pairs of W_0. Thus there is an additional degeneracy in W_∞ due to the possibility of the presence or absence of this central node in x; when this node is absent the electronic state of the molecule is called symmetric, when present the state is called antisymmetric with respect to the nuclei.

As the nuclei are brought together the total quantum number n changes from $(n_\eta+n_\phi+n_\xi+1)$ to $(n_\eta+n_\phi+2n_\xi+1)$ for the symmetric case or to $(n_\eta+n_\phi+2n_\xi+2)$ for the antisymmetric, and therefore n changes in value unless $n_\xi=0$ and the molecule is symmetric. Such an increase in n is called promotion. The maximum promotion possible is a doubling of n and occurs when $n_\eta=n_\phi=0$ and the molecule is antisymmetric. In this case $W_0=W_\infty$.

The energy levels for $0<\rho<\infty$ will be labelled by the new Hund notation,[6] the number indicating the value of $n(=n_y+n_\phi+n_x+1)$ the Roman letter (in the sequence s, p, d, f, g, $\cdots$,) indicating the value of n_x+n_ϕ, and the Greek letter (in the sequence σ, π, δ, ϕ, γ, $\cdots$,) indicating the value of n_ϕ. Thus a $3d\pi$ state is one in which $n=3$, $n_y=0$, $n_\phi=1$, and $n_x=1$. Since n and n_x undergo a change in value for $\rho=\infty$, but n_ϕ does not, the important letter in the label is the Greek one.

The connections between the W_0 and W_∞ labels can thus be calculated by the above formulas and labels can be given each connecting energy curve. It is perhaps well to consider several simple examples of this nodal argument in connecting the W_0 and W_∞ levels. The task is to follow the changes in the nodal surfaces as ρ goes from zero to infinity or vice versa.

The normal state of the united atom, He^+, has no nodal surfaces, and its energy is $4R$. When the nuclei are separated the wave function separates into two portions, each concentrated about a nucleus, and each of the same sign. Therefore when $\rho=\infty$ there will still be no nodal surface and the energy of the system will be that of the normal state of the hydrogen atom, R. This energy curve $4R \rightarrow R$ is labelled the $1s\sigma$ state.

When $n=2$ for the united atom the energy is R and there are three possibilities for the one nodal surface. It can be in r, in which case the nodal surface is a sphere. Then when $\rho>0$, $r \rightarrow \rho y$ and the sphere becomes an ellipsoid. When $\rho=\infty$ the ellipsoid becomes two paraboloids, one about each nucleus, and so there is still a nodal surface near each nucleus, and the energy level for the separated atom is the second hydrogen atom level, $R/4$. This state is labelled $2s\sigma$.

If the nodal surface is in ϕ, the surface will still be through each nucleus when $\rho=\infty$, and so this state, called the $2p\pi$, also has an energy going from R to $R/4$.

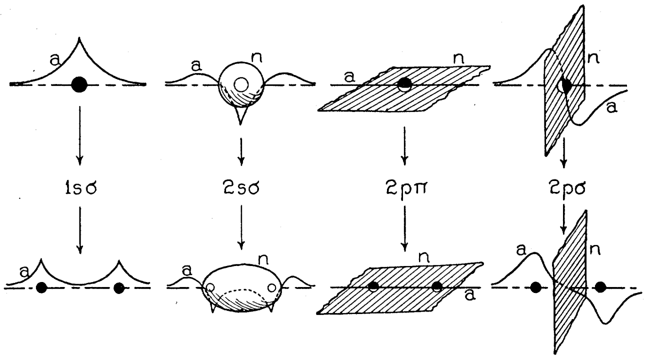

Fig. 1. Behavior of the nodal surfaces. Small circles represent the nuclei, shaded surfaces n the nodal surfaces and curves a the values of ψ along the axis.

If, however, the node is in θ, then when $\rho>0$, the two nuclei will separate, leaving the nodal plane halfway between them and perpendicular to the nuclear axis. When $\rho=\infty$ this plane will be an infinite distance from either nucleus, and the energy of the system is R, that of a hydrogen atom in the normal state. This state is called the $2p\sigma$ state, and when $\rho=\infty$ it differs from the $1s\sigma$ state only in the fact that the wave function about the two nuclei are of opposite sign. In other words, the $1s\sigma$ state corresponds to the symmetric case and the $2p\sigma$ state to the antisymmetric.

Figure 1 shows these four states and the change in the nodal surfaces. The value of the wave function along the nuclear axis is also given.

The general study above developed will show that the following levels for separated and united atoms must be connected by curves.

It should be noted that states where the Greek and Roman letters are the same are unpromoted states, for a difference between the two letters would indicate a node in x, and these nodes are the ones which cause promotion. It should also be noted that this scheme differs from that which Hund published at first,[3] but coincides with his latest scheme.[6]

TABLE I

United Atom		Molecule		Separated Atom	
Energy	Quantum No. for He^+	Quantum No. for H_2^+	State	Quantum No. for H	Energy
	$n\ n_r n_\phi n_\theta$	$n\ n_y n_\phi n_x$		$n\ n_\eta n_\phi n_\xi$	
$4R$	1000	1000	$1s\sigma$	1000	R
R	2001	2001	$2p\sigma$ (promoted)	1000	R
R	2010	2010	$2p\pi$	2010	$R/4$
R	2100	2100	$2s\sigma$	2100	$R/4$
$4R/9$	3101	3101	$3p\sigma$ (promoted)	2100	$R/4$
$4R/9$	3002	3002	$3d\sigma$ (promoted)	2001	$R/4$
$4R/9$	3011	3011	$3d\pi$ (promoted)	2010	$R/4$
$4R/9$	3020	3020	$3d\delta$	3020	$R/9$
$4R/9$	3110	3110	$3p\pi$	3110	$R/9$
$4R/9$	3200	3200	$3s\sigma$	3200	$R/9$
$R/4$	4003	4003	$4f\sigma$ (dbly. prom.)	2001	$R/4$
$R/4$	4102	4102	$4d\sigma$ (promoted)	3101	$R/9$
$R/4$	4201	4201	$4p\sigma$ (promoted)	3200	$R/9$
$R/4$	4012	4012	$4f\pi$ (promoted)	3011	$R/9$
$R/4$	4111	4111	$4d\pi$ (promoted)	3110	$R/9$
$R/4$	4021	4021	$4f\delta$ (promoted)	3020	$R/9$
$R/4$	4030	4030	$4f\phi$	4030	R/16
$R/4$	4120	4120	$4d\delta$	4120	$R/16$
$R/4$	4210	4210	$4p\pi$	4210	$R/16$
$R/4$	4300	4300	$4s\sigma$	4300	$R/16$

Any approximate quantitative values obtained for the various energies as functions of ρ must be joined so that they satisfy the requirements of this scheme.

PERTURBATION METHOD I

There are two different methods of obtaining these approximate values. The first is to consider the wave function of the molecule to be that of the united atom, Ψ_0, in the first approximation, and to study the perturbation of the energy levels of the united atom when ρ is made greater than zero. The perturbing energy will be the difference between the potential field due to the united nuclei and the field due to the two nuclei a small distance 2ρ apart. This method will not be valid for large values of ρ, values, say, larger than $a/2$, but it will serve to indicate how the various degenerate levels of the united atom split.

A slightly better approximation is to consider as the unperturbed wave function not the Ψ_0 for the He^+ ion with $Z=2$, but a wave function for an ion with such a Z' that the first order perturbation of the corresponding energy, due to the separation of the nuclei and increase of their joint charge to $2e$, is zero. This has the effect of increasing the spread of the unperturbed wave function, and although this "stretching" is spherically symmetric, it approximates the true wave function better than the "unstretched" function.

The function used is that in Eq. (3) with Z changed to Z' and a_0 to a_0', and Z' left undetermined for the time being.

The theory of perturbations of a degenerate system[14] is that the various perturbations of the energy levels W resulting from one degenerate level $W_0(n)$ are to be found by the equation

$$\begin{vmatrix} (W_{nlm}^{nlm}-W) & W_{nlm}^{nlm'} & W_{nlm}^{nl'm'} & \cdots \\ W_{nlm'}^{nlm} & (W_{nlm'}^{nlm'}-W) & W_{nlm'}^{nl'm'} & \cdots \\ W_{nl'm'}^{nlm} & W_{nl'm'}^{nlm'} & (W_{nl'm'}^{nl'm'}-W) & \cdots \\ \cdot & \cdot & \cdot & \cdots \\ \cdot & \cdot & \cdot & \cdots \end{vmatrix} = 0 \qquad (7)$$

where n is the principal quantum number, and l, l', m and m' are various values of the quantum numbers with respect to which the system is degenerate; and where

$$W_{nl'm'}^{nlm} = \int \Psi_0(nlm) \cdot \bar{\Psi}_0(nl'm') \cdot V_1 dv$$

where dv is the volume element and V_1 is the perturbation of the potential energy. The actual energy $W(nrs)$ of any one of these resultant levels is then $W_0(n)$ plus one of the roots of Eq. (7). If all the non-diagonal terms of the type $W_n{}^n{}_{l'}{}^l{}_{m'}{}^m$ and $W_n{}^n{}_l{}^{l'}{}_m{}^{m'}$, are zero for a particular l and m then the root corresponding will be $W = W_n{}^n{}_l{}^l{}_m{}^m$, and r and s can be indentified with the quantum numbers l and m of the unperturbed wave function. Otherwise r and s cannot be identified with l and m, but represent quantum numbers corresponding to a new coordinate system. In other words, if the coordinate system for the perturbed function is in the first approximation equal to the principal coordinate system for the unperturbed function then r and s can be identified with l and m. But if these two coordinate systems are not equal in the first approximation then the two quantum number sets cannot be identified and non-diagonal terms appear in the above determinant. The problem is to choose a coordinate system for the unperturbed function by proper combination of the wave functions such that this determinant is all diagonal, and failing this, to make it have as few non-diagonal terms as possible.

In the case considered, symmetry shows that sperical coordinates are the best ones to use for Ψ_0. The perturbing energy

$$V_1 = (Z'e^2/r) - (Ze^2/2r_1) - (Ze^2/2r_2)$$

Here $Z = 2$ and Z' will be determined later to make the perturbation energy zero. These last terms can be expanded in a series of Legendre polynomials, and

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[14] E. Schroedinger, Ann. d. Physik **80**, 452 (2926).

$$V_1\begin{cases} =\dfrac{Z'e^2}{r}P_0-\displaystyle\sum_{\alpha=0}^{\infty}\dfrac{Ze^2\rho^{2\alpha}}{r^{2\alpha+1}}P_{2\alpha}(\cos\theta) & \text{when} \quad r>\rho \\ =\dfrac{Z'e^2}{r}P_0-\displaystyle\sum_{\alpha=0}^{\infty}\dfrac{Ze^2r^{2\alpha}}{\rho^{2\alpha+1}}P_{2_\infty}(\cos\theta) & \text{when} \quad r<\rho. \end{cases} \tag{8}$$

Using the unperturbed wave function from Eq. (3), the perturbation energy becomes a function of n, l, l' and m, ρ and $a_0'(=a/2Z')$, namely, $W_n{}^n{}_l{}^{l'}{}_m{}^m$

Since the angle ϕ only enters in the $e^{im\phi}$ factor the above energy cannot be non-diagonal in m and the only non-diagonal terms possible will be those in l as is shown. An application of the recurrence formulas of the type:

$$P_0P_l{}^m=P_l{}^m$$

$$P_2P_l{}^m=\frac{1}{2(2l-1)(2l+1)(2l+3)}[3(2l+3)(l+m)(l+m-1)P_{l-2}^{m} \tag{9}$$

$$+2(2l+1)(l^2+l-3m^2)P_l{}^m+3(2l-1)(l-m+1)(l-m+2)P_{l+2}^{m}]$$

etc.

shows that $W_n{}^n{}_l{}^{l'}{}_m{}^m$ (for $l\neq l'$) is zero unless $l=l'+2s$ where s is an integer. This can only happen when n is 3 or greater and therefore there will be no non-diagonal terms in the first two levels, and but one pair when $n=3$.

The expressions for these energies were calculated for the first three values of n and the exponentials expanded to give a series in $c=d/a=2\rho/a$, the distance between the nuclei in terms of the first Bohr orbit of the hydrogen atom as a unit. For instance

$$W_{100}^{100}=R\left[8e^{-2cZ'/Z}\left(\frac{Z'}{Z}+\frac{1}{c}\right)-(8/c)+8(Z'/Z)^2\right]$$

is expanded into a series in c, and the perturbed energy

$$W(1s\sigma)=R[8g-4g^2-16c^2g^3/3+16c^3g^4/3-16c^4g^5/5+64c^5g^6/45+\cdots]$$

where $g=Z'/Z$. In this lowest state the series converges quite slowly and is not as well adapted for calculation as the actual energy expression. For the higher states, however, the series is a satisfactory approximation of the complicated set of exponentials in the actual expression, and is simpler than it.

The quantity $g(=Z'/Z)$ is adjusted so that $W_{100}^{100}=0$ for a given c. Then the energy $W(1s\sigma)=4Rg^2$ is equal to the perturbed energy for the particular value of c chosen. This method "stretches" the wave function as discussed earlier. However, in the higher states, especially when $n>2$, the difference $1-g$ is very small, and it is then easier and nearly as accurate to set $g=1$ and compute the resulting value of $W_n{}^n{}_l{}^l{}_m{}^m$ as a function of c, and add it to $W_0(n)=4R$ to obtain the perturbed energy.

The series for the various perturbed energies for the higher states are tabulated in Table II as functions of c.

TABLE II.

$$W(2p\sigma)=R[2g-g^2+2g^3c^2/15-9g^5c^4/140+7g^6c^5/180+\cdots]$$

$$W(2p\pi)=R[2g-g^2-g^3c^2/15+g^5c^4/140-g^6c^5/180+\cdots]$$

$$W(2s\sigma)=R[2g-g^2-2g^3c^2/3+2g^4c^3/3-7g^5c^4/20+11g^6c^5/90+\cdots]$$

$$W(3p\sigma)=R\left\{\frac{4}{9}+\frac{16e^{-2c/3}}{405}[c^2+2c^3/3-22c^4/\ 63+\ 8c^5/567+\cdots]\right\}$$

$$W(3d\pi)=R\left\{\frac{4}{9}+\frac{8e^{-2c/3}}{2835}[c^2+2c^3/3+20c^4/163-\ 4c^5/\ 81+\cdots]\right\}$$

$$W(3d\delta)=R\left\{\frac{4}{9}-\frac{16e^{-2c/3}}{2835}[c^2+2c^3/3+17c^4/\ 81+10c^5/729+\cdots]\right\}$$

$$W(3p\pi)=R\left\{\frac{4}{9}-\frac{8e^{-2c/3}}{405}[c^2+2c^3/3+2\ c^4/\ 21+\ 8c^5/567+\cdots]\right\}$$

The two states having a non-diagonal term are

$$W_{320}^{320}=R\frac{32e^{-2c/3}}{2835}[c^2+2c^3/3+8c^4/9+8c^5/27+\cdots]$$

$$W_{300}^{300}=-R\frac{16e^{-2c/3}}{81}[c^2-c^3/3+c^4/15+0+\cdots]$$

$$W_{300}^{320}=R\frac{8e^{-2c/3}}{225(2)^{1/2}}[19c^2/9-8c^3/27-16c^4/567-4c^5/1601+\cdots].$$

And the resulting energy levels are

$$W(3s\sigma)=4R/9+\frac{(W_{300}^{300}+W_{320}^{320})}{2}+\left[\frac{(W_{300}^{300}-W_{320}^{320})^2}{4}+(W_{300}^{320})^2\right]^{1/2}$$

$$W(3d\sigma)=4R/9+\frac{(W_{300}^{300}+W_{320}^{320})}{2}-\left[\frac{(W_{300}^{300}-W_{320}^{320})^2}{4}+(W_{300}^{320})^2\right]^{1/2}$$

The values of the energies in units of R are given in Table III for five values of c.

TABLE III

State \ c	0	0.25	0.50	0.75	1.00
$1s\sigma$	4.000	3.742	3.318	3.015	2.750
$2p\sigma$	1.000	1.008	1.031	1.065	1.120
$2p\pi$	1.000	.996	.980	.955	.921
$2s\sigma$	1.000	.968	.910	.861	.822
$3p\sigma$	.444	.446	.453	.462	.471
$3d\sigma$	.444	.445	.449	.455	.465
$3d\pi$	.444	.444	.446	.447	.450
$3d\delta$	.444	.444	.443	.441	.439
$3p\pi$	.444	.443	.439	.434	.428
$3s\sigma$	.444	.434	.412	.387	.363

Notice that the sequence of the levels does not agree with that given by Hund[3,6] for small values of nuclear separation. Hund's sequence, however, was obtained by a purely qualitative process, and so is likely to be in error. Furthermore the calculations here have assumed no relativity or spin fine structure separation of the levels in the excited levels in the united atom. This would impose a different sequence of very small energy differences for very small values of c; but this sequence would soon be wiped out, for the sequence given above would soon become the predominating one.

Notice also that the energies of all the promoted states are perturbed downward (i.e., these energies become larger numerically) and those of the unpromoted states are perturbed upward.

PERTURBATION METHOD II

The second method of obtaining approximate values of the energy as a function of ρ is a modification of the method used by Heitler and London,[15] utilizing the fact that Ψ is known for $\rho=\infty$, and has been given by Eq. (6). It can be assumed that to the first approximation Ψ retains its form as ρ is made "less than" infinity. The change in the energy levels will be due to the slight effect of the distant nucleus on the electron. When the electron is about the first nucleus the perturbing energy is e^2Z_∞/r_2, and when about the second nucleus is e^2Z_∞/r_1. Thus when $\Psi\overline{\Psi}\ V_1dv$ is integrated in the range $-1\leqq x\leqq 0$, V_1 is $-Z_\infty e^2/r_2=-Z_\infty e^2/\rho(y-x)$, and in the range $0\leqq x\leqq +1$ it is $-Z_\infty e^2/r_1=-Z_\infty e^2/\rho(y+x)$.

When $\rho<\infty$ the normalizing factor is no longer N_∞, and the best way to determine it is by actual integration. From Eq. (4), $(N_\rho)^{-2}=\frac{1}{2}\int\psi_1{}^2dv+\frac{1}{2}\int\psi_2{}^2dv\pm\int\psi_1\psi_2dv$. But the first terms are equal and so $(N_\rho)^{-2}=\int\psi_1{}^2dv\pm\int\psi_1\psi_2dv=N_A\pm N_B$, for convenience, where, if $b=\rho/na_\infty$, $u=yb$ and $v=xb$

$$N_A=2\pi(na_\infty)^3\int_1^\infty[2(u-b)]^m\cdot e^{-u}\cdot[L_{n-k-1}^{m}(2u-2b)]^2\cdot du$$
$$\cdot\int_{-1}^{1}(u^2-v^2)\cdot[2(b+v)]^m\cdot e^{-v}\cdot[L_{k+m}^{m}(2b+2v)]^2dv \tag{10}$$

$$N_B=2\pi(na_\infty)^3\int_1^\infty[2(u-b)]^m\cdot e^{-u}\cdot[L_{n-k-1}^{m}(2u-2b)]^2\cdot du$$
$$\cdot\int_{-1}^{1}(u^2-v^2)[4(b^2-v^2)]^{m/2}\cdot L_{k+m}^{m}(2b+2v)\cdot L_{k+m}^{m}(2b-2v)\cdot dv. \tag{11}$$

Similarly the integral

$$\begin{aligned}V_1dv=V_A\pm V_B=-2\pi e^2Z(na_\infty)^2&\int_1^\infty[2(u-b)]^m\cdot e^{-u}\cdot[L_{n-k-1}^{m}(2u-2b)]^2\cdot du\\ \cdot\int_{-1}^{1}&\{(u-v)\cdot[2(b+v)]^m\cdot e^{-v}\cdot[L_{k+m}^{m}(2v+2b)]^2\\ &+(u-v)[2(b-v)]^m\cdot e^{+v}\cdot[L_{k+m}^{m}(2b-2v)]^2\\ &\pm 2(u-v)[4(b^2-v^2)]^{m/2}\cdot L_{k+m}^{m}(2b+2v)\cdot L_{k+m}^{m}(2b-2v)\}dv\end{aligned} \tag{12}$$

and the perturbed energy is thus

$$\begin{aligned}W(n,k,m)&=W_\infty(n)+V_A/(N_A\pm N_B)\pm V_B/(N_A\pm N_B)\\ &=W_\infty(n)+A\pm B.\end{aligned}$$

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[15] Heitler and London, Zeits. f. Physik **44**, 455, (1927).

The plus sign is taken for the symmetric case and the minus for the antisymmetric.

The non-diagonal terms in the energy determinant of Eq. (7) are all zero here, for the wave functions have been so chosen that $\psi_1/(r_2)^{1/2}$ is orthogonal for different values of n, k and m, and the integral of the product of a symmetric and antisymmetric Ψ gives the difference between two equivalent integrals, and is thus also zero.

The perturbed energies $W(n,k,m)$ have been calculated for the states $n=1$ and $n=2$ as functions of c. They are given in Table IV.

TABLE IV

$$W(1s\sigma)=R\left[1+\frac{4}{c}\cdot\frac{2+(c^2+2c+2)e^{-c}}{4+(4c^2/3+4c+4)e^{-c}}\right]$$

$$W(2p\sigma)=R\left[1+\frac{4}{c}\cdot\frac{2-(c^2+2c+2)e^{-c}}{4-(4c^2/3+4c+4)e^{-c}}\right]$$

$$W(2s\sigma)=R\left[\frac{1}{4}+\frac{4-2e^{-c}-2e^{-c/2}+(c^2/4+3c)e^{-c/2}}{(2c+6)-(c+6)e^{-c}+(c^3/12+3c^2/2+7c)e^{-c/2}}\right]$$

$$W(3p\sigma)=R\left[\frac{1}{4}+\frac{4-2e^{-c}-2e^{-c/2}-(c^2/4+3c)e^{-c/2}}{(2c+6)-(c+6)e^{-c}-(c^3/12+3c^2/2+7c)e^{-c/2}}\right]$$

$$W(3d\sigma)=R\left[\frac{1}{4}+\frac{4+(2c+2)e^{-c}-(c^2/2+2c+6)e^{-c/2}+(5c^4/96-c^3/12-3c^2/4+c)e^{-c/2}}{(2c-6)+(c^2+5c+6)e^{-c}+(c^5/60-c^3/4-c^2/2+c)e^{-c/2}}\right]$$

$$W(4f\sigma)=R\left[\frac{1}{4}+\frac{4+(2c+2)e^{-c}-(c^2/2+2c+6)e^{-c/2}-(5c^4/96-c^3/12-3c^2/4+c)e^{-c/2}}{(2c-6)+(c^2+5c+6)e^{-c}-(c^5/60-c^3/4-c^2/2+c)e^{-c/2}}\right]$$

$$W(2p\pi)=R\left[\frac{1}{4}+\frac{1}{2c}\cdot\frac{8-2ce^{-c}-(2c+8)e^{-c/2}+(\pi c^3/8-c^3/6+\pi c^2/8)e^{-c/2}}{2-(c/2+2)e^{-c}+(3\pi c^3/256+\pi c^2/8+3\pi c/8)e^{-c/2}}\right]$$

$$W(3d\pi)=R\left[\frac{1}{4}+\frac{1}{2c}\cdot\frac{8-2ce^{-c}-(2c+8)e^{-c/2}-(\pi c^3/8-c^3/6+\pi c^2/8)e^{-c/2}}{2-(c/2+2)e^{-c}-(3\pi c^3/256+\pi c^2/8+3\pi c/8)e^{-c/2}}\right]$$

The values of these energies in units of R are given for several values of c in Table V.

TABLE V

State \ c	3	4	5	7.5	10	20	∞
$1s\sigma$	1.702	1.516	1.405	1.269	1.200	1.100	1.000
$2p\sigma$	1.454	1.442	1.377	1.260	1.200	1.100	1.000
$2p\pi$	.698	.619	.555	.475	.450	.350	.250
$2s\sigma$	.642	.572	.508	.455	.400	.337	.250
$3p\sigma$	.443	.428	.421	.408	.400	.337	.250
$3d\sigma$	.671	.712	.700	.618	.520	.367	.250
$3d\pi$	.575	.580	.550	.475	.450	.350	.250
$4f\sigma$	.524	.610	.571	.550	.520	.367	.250

The calculations become invalid for small values of c since the wave function in this case is no longer even approximately like that for $c=\infty$. Due to the character of the wave function it should be expected that the calculations for the promoted states will cease to be valid at a larger c than those for the unpromoted states. In no case, however, should it be expected that this perturbation method be valid for c less than 3 or 4. Several curves when extended to $c=1$ coincided almost exactly with the value of the energy calculated by method I. This was considered fortuitous however, for several other curves gave wide discrepancies at $c=1$.

So the method used was to plot the curves obtained by method I from $c=0$ to $c=1$, and those obtained by method II from $c=3$ to $c=\infty$, and to fill in the intermediate gaps by a smooth curve. In case of any doubt as to which curve joins which, the nodal reasoning discussed earlier is the criterion used.

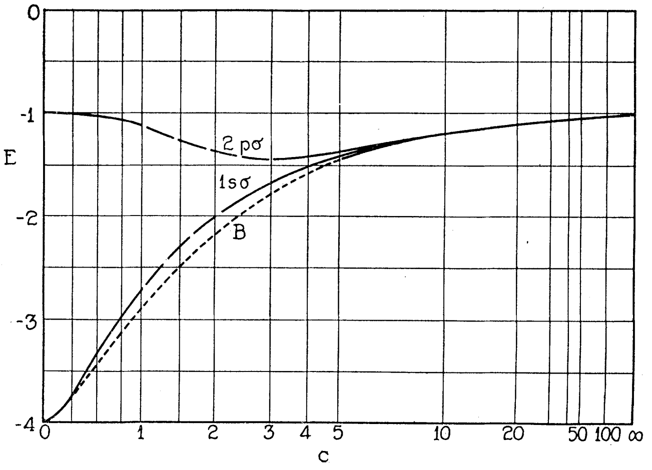

Fig. 2. Electronic energy curves for lowest two states.

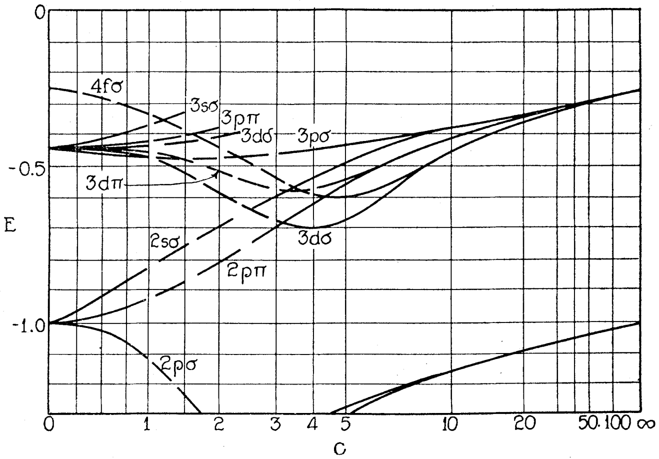

Fig. 3. Electronic energy curves for upper states.

Fig. 2 shows curves for the $1s\sigma$ and $2p\sigma$ states. The abscissa is in terms of $10c/(c+5)$ in order to get the whole range $0 \leqq c \leqq \infty$ in the figure. The ordinate is in terms of R. The solid lines represent the parts of the curves which could be calculated, and the intermediate dashed lines represent the extrapolated portions. The dotted line below the $1s\sigma$ curve is that calculated by Burrau for this same state and is probably fairly correct throughout the whole range of c. This is the only independent check available for the curves, but the good agreement indicates that the other curves are not far from the actual values.

Fig. 3 shows the curves for the other levels on a magnified energy scale.

These curves are but the electronic energies as functions of c. The potential energy $V(nlm)$ of the molecule is the electronic energy plus the energy of repulsion of the nuclei $E_n = Z_\infty{}^2e^2/d$. Potential energy curves for all the various states are shown in Fig. 4.

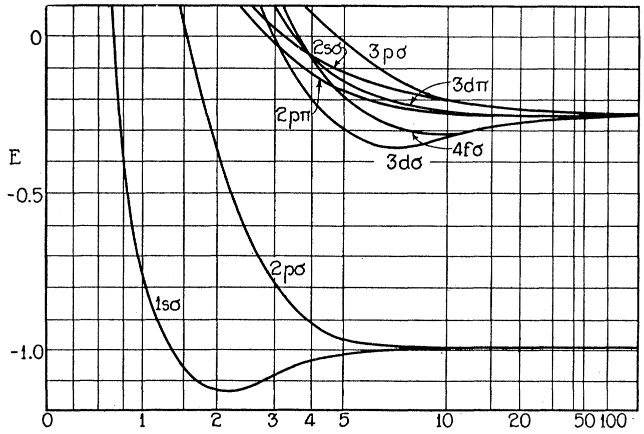

Fig. 4. Potential energy curves.

Only three of these curves show minima, those corresponding to the $1s\sigma$, the $3d\sigma$ and the $4f\sigma$ states. Therefore to this degree of approximation the molecule $H_2{}^+$ is only stable in these three states of all the ones considered. The other states, with their curves, cannot be considered as having no meaning however, for transitions from stable to unstable states have been used to explain certain experimental results.[16,17]

The value of V at the minimum point shall be called $V_m(nlm)$, and the value of c at the minimum shall be $c_m(nlm)$. The values of the calculated V_m are

$$V_m(1s\sigma) = 1.142R = 15.49 \text{ volts}$$

$$V_m(3d\sigma) = 0.350R = 4.74 \text{ volts}$$

$$V_m(4f\sigma) = 0.309R = 4.19 \text{ volts}.$$

The energy of dissociation $E_D(nlm)$ is the difference $W_\infty - V_m$, and has the values

$$E_D(1s\sigma) = 0.142R = 1.93 \text{ volts}$$

$$E_D(3d\sigma) = 0.100R = 1.35 \text{ volts}$$

$$E_D(4f\sigma) = 0.059R = 0.80 \text{ volts}.$$

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[16] Winans and Stueckelberg, Proc. Nat. Acad. **14**, 867 (1928).

[17] Smyth and Condon, Proc. Nat. Acad. **14**, 871 (1928).

The value for the normal state agrees fairly well with the one experimentally determined value available. This value is the ionization potential of H_2, which is 16.1v.[18] The value given here would be the ionization potential of H, 13.5v, plus the dissociation energy of H_2, 4.3v, minus the difference between W_∞ and the $1s\sigma$ curve at $c=1.6$ (the equilibrium separation of the H_2 normal state), 1.5v, giving a value of 16.3v as ionization potential of H_2 expected from these curves.

The values of c_m are

$$c_m(1s\sigma)=2.1a=1.12\times 10^{-8}\text{ cm}$$
$$c_m(3d\sigma)=7.6a=4.10\times 10^{-8}\text{ cm}$$
$$c_m(4f\sigma)=9.4a=5.06\times 10^{-8}\text{ cm}.$$

These values of c may differ considerably from the correct values, since all three minima fall on the portion of the curve which is least accurately known. It is possible that the true values are all somewhat smaller than those calculated.

There are few experimental data available to check these curves. C. J. Brasefield is at present making measurements on the electronic bands corresponding to these levels, and so an experimental check should be forthcoming shortly.

The results above have been rather surprising, since it has been expected that all unpromoted states have minima and that no promoted state could have a minimum.[7] There has been no theoretical justification for this expectation, however, and the above results show it to be erroneous. For even if the minima for the two promoted states $3d\sigma$ and $4f\sigma$ are not actually as deep as these first approximations indicate, the curves for both these states start downward as c is decreased from infinity, and at $c=20$, where the first approximation should still give fairly accurate results, the energy for these two states is definitely below the value of W_∞; thus showing that they must have a minimum point and a finite c_m. It seems fairly certain that the pair of states $2s\sigma$ and $3p\sigma$ have no minimum, for the energy curves corresponding to these states are above W_∞ for every finite value of c. Thus two promoted states, $3d\sigma$ and $4f\sigma$, have minima, and one unpromoted state, $2s\sigma$, has no minimum.

However the energies for the levels $2p\pi$, $3d\pi$ remain practically equal to W_∞ throughout the range $\infty \geqq c > 10$, and a second approximation may show that these states have slight minima. But these minima, if they exist, will have large values of c_m and small values of E_D, and so will be relatively unstable.

No determination was made of the size of the second or higher orders of approximation, due to the prohibitive difficulty of such calculations. There is no proof that the method of successive approximations used above gives such a rapidly converging series that the first term is sufficient or even in-

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[18] E. Franck und P. Jordan, Anregung von Quantensprüngen Hand. d. Phys. XXIII. Springer, Berlin (1926).

dicative, except that in the cases where calculation by other methods and where experimental data were available these first terms checked fairly well.

Work is being carried on by V. Guillemin and C. Zener to obtain these same curves by a completely different method of approximation. It will greatly strengthen belief in the general validity of the wave-mechanical perturbation methods if these new curves check the ones presented above.

Having now obtained the energy curves for one electron, the problem of the many electron diatomic molecule can be attacked next. For instance, the hydrogen molecular electronic energy can be considered as being due to the sum of the individual electronic energies as given above, plus the energy of interaction between the electrons. The writers are calculating a set of curves of this type.

The authors wish to express their appreciation of the aid rendered by Professor E. U. Condon in the preparation of this paper.

Palmer Physical Laboratory,
Princeton University,
February, 1929.