

Redundant Zeros in the Discrete Energy Spectra in Heisenberg's Theory of Characteristic Matrix

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AN important recent development in Heisenberg's theory of characteristic matrix is the determination of discrete energy values of closed stationary states.¹ This is made possible by the process of analytic continuation from real values of the momentum variables to imaginary values in the complex plane. Those imaginary values for which the amplitude of the outward scattered wave vanishes correspond to the closed stationary states and the corresponding negative energy values can be identified with the energy values of these states. It has been pointed out by Pauli that this procedure gives correct results for the scattering by a potential hole and the scattering by an attractive Coulomb field. Using this method, the writer has studied the case of an attractive exponential field, which presents a certain new feature.

We consider the spherically symmetrical state in the field

$$V(r) = -V_0 e^{-r/a},$$

where V_0 and a are positive constants. Let $u(r)/r$ be the wave function and E the energy of the scattered particle, which is positive. If we write

$$V_0 = \frac{\hbar^2}{2m} U_0, \quad E = \frac{\hbar^2 k^2}{2m},$$

the wave equation takes the form

$$(d^2u/dr^2) + (k^2 + U_0 e^{-r/a})u = 0.$$

The solutions of this equation are

$$u = J \pm 2aki(2a(U_0 x)^{\frac{1}{2}})$$

where the J 's are Bessel functions and $x = e^{-r/a}$. The condition that the function u should vanish at the origin requires it to be of the form

$$u = c[J - 2aki(2a(U_0)^{\frac{1}{2}})J_{2aki}(2a(U_0 x)^{\frac{1}{2}}) - J_{2aki}(2a(U_0)^{\frac{1}{2}})J - 2aki(2a(U_0 x)^{\frac{1}{2}})],$$

where c is a constant. The asymptotic expression for large values of r is

$$u = c[J_{-2aki}(2a(U_0)^{\frac{1}{2}})(a(U_0)^{\frac{1}{2}})^{2aki} e^{-ikr} / \Gamma(2aki + 1) - J_{2aki}(2a(U_0)^{\frac{1}{2}})(a(U_0)^{\frac{1}{2}})^{-2aki} e^{ikr} / \Gamma(-2aki + 1)].$$

From this asymptotic expression it can be seen that, as usual, there is no closed state when k is real. When k becomes imaginary, however, the above general consideration leads to the following conditions for closed states:

$$\begin{aligned} J_{2aki}(2a\sqrt{U_0}) &= 0, & (i) \\ 1/\Gamma(-2aki + 1) &= 0. & (ii) \end{aligned}$$

The first condition gives the discrete spectrum obtained by Bethe.² The second condition gives

$$-2aki + 1 = -n \quad (n = 0, 1, 2, \dots)$$

or

$$E = -\hbar^2(n+1)^2/8ma^2.$$

These eigenvalues do not correspond to any actual closed states. They may therefore be regarded as redundant zeros.

This special problem is of some interest in connection with the general formulation of the method for determining closed stationary states, as in Heisenberg's new theory there is no longer a wave equation to determine the wave function completely and consequently some other criterion is necessary for discarding such redundant zeros as are given by condition (ii).

¹ Møller, Kgl. Danske Vid. Sels., Math.-Fys. Medd. 23, No. 1 (1945).
² Bethe and Bacher, Rev. Mod. Phys. 8, 111 (1936).

Physical Interaction of Electrons with Liquid Dielectric Media. The Properties of Metal-Ammonia Solutions

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THE author wishes to outline briefly the primitive theoretical considerations which preceded recent experimental discoveries relating to the properties of metal-ammonia solutions.¹ The basis of the treatment is the model, first proposed by Kraus,² of an electrolyte-like character for the solute metal in ammonia solutions, the negative ion constituent being the "solvated" electron. At extremely low concentrations, inter-ionic forces may be neglected. It is proposed that under these conditions individual electrons are "self-trapped" in physical cavities created in the solvent medium. If surface tension effects are neglected, the potential energy is due only to electrical polarization of the medium surrounding the cavity. The dielectric constant D of ammonia is sufficiently large (~ 22) so that without serious error the term $1/D$ may be neglected in comparison with unity in the well-known Born expression for the polarization energy. Hence as a first approximation, for a charge Ze symmetrically distributed in a spherical cavity of radius r_0 , the potential energy

$$V = -Z^2 e^2 / 2r_0, \quad r < r_0; \quad V = 0, \quad r > r_0.$$

The attractive force, tending to shrink the cavity, is opposed by an especially simple quantum-effect repulsion. In essence, the magnitude of the de Broglie wave-length must correspond to the cavity diameter, leading to a zero-point kinetic energy. As a first approximation, the wave function is considered to have a node at the cavity boundary. The problem then reduces to that of a particle in a spherical box.³ Solution of the Schrödinger equation yields for the lowest s state the kinetic energy $T = \hbar^2 / 8mr_0^2$. Hence the total energy $W = T + V = (\hbar^2 / 8mr_0^2) - (e^2 / 2r_0)$. Setting dW/dr_0 equal to zero, the equilibrium values of W and r_0 are found to be, respectively, $-(me^4 / 2\hbar^2)$ (i.e., some -0.38 electron volt) and $\hbar^2 / 2me^2$ (i.e., some 9.9×10^{-8} cm). The corresponding experimental values¹ are approximately -0.8 volt and 7×10^{-8} cm. Consideration of the finite "depth" of the potential well, with resultant penetration of the wave function outside the cavity (requiring a self-consistent field method) should improve the agreement

with experiment. A more accurate treatment should also include the effect of something resembling surface tension of the (probably diffuse) cavity wall.

Extending the simplified particle-in-a-spherical-box treatment to a system of *two* 1s electrons trapped in a cavity, application of first-order perturbation theory yields

$$W = \frac{\hbar^2}{4\pi r_0^2} - \frac{2e^2}{r_0} + \int \frac{e^2}{r_{12}} \psi_0^2 dT.$$

The third term (involving the unperturbed wave functions and the separation r_{12} of the electrons) corresponds to electrostatic repulsion between the electrons, and is evaluated by adaptation of the analogous treatment for the normal helium atom.⁴ By numerical methods, its value approximates to $+e^2/r_0$. The corresponding approximate values of r_0 and W would be $\hbar^2/2me^2$ and $-me^4/\hbar^2$. From physical analogy with the helium atom like problem, it appears that higher approximations would yield a value of W numerically *greater* than me^4/\hbar^2 . (For example, first order perturbation treatment gives for hydride ion⁴ $W = -0.75 W_H$, while variation methods yield $W = -1.05 W_H$.) The above theoretical trapping energy for a single electron is $-me^4/2\hbar^2$. That is, the trapped pair should be stable with respect to dissociation into two electrons trapped in separate cavities. This at first sight paradoxical result arises from the greatly increased polarization energy of the pair (*vide* the factor Z^2 in the Born formula) which more than compensates for electrostatic repulsion. It appears highly probable that this energetic stability of the pair would be retained by a more accurate treatment (i.e., one considering the penetration of the wave functions outside the cavity). The Pauli exclusion principle requires the trapped pair to be in a singlet state—i.e., to be diamagnetic.

The hitherto neglected inter-ionic forces become increasingly important with greater solute concentration. In the limit, the electrostatic attractive potential on a cluster of Z electrons at average distance ρ from singly charged positive ions approaches $-AZ(e^2/\rho)$. The Madelung constant A for random configuration should have a value of the order of magnitude of 1.5, and hence this potential can become (for $Z=1$) much larger than the polarization potential $-Z^2e^2/2r_0$. One result is a greatly decreased value of the radius of the electron cavity—the molar volume in concentrated solutions of sodium is about 40 cm³, as compared with some 700 cm³ for highly dilute solutions. Further, the linear dependence on Z gives no appreciable energetic advantage to the pairing of electrons, and their mutual repulsion would render the pairs unstable. This unpairing of electrons in concentrated solutions is indicated by the reappearance of appreciable paramagnetic susceptibility, as contrasted with diamagnetism of the solute at intermediate concentrations.

Extension of the "particle in a box" treatment indicates that the kinetic energy of a trapped electron excited to a p state exceeds the potential energy of the s ground state. By the Franck-Condon principle a continuous absorption spectrum should result, leading to photo-ejection of the electron from the cavity. The infra-red absorption maxi-

mum of very dilute metal-ammonia solutions corresponds to transition to the first p state. Current experimental studies reveal a far ultraviolet absorption maximum, corresponding to transition to the second p state. The theory of the continuous absorption spectrum of the trapped pair is developed in like fashion.

The theory as outlined applies in essential detail to any solvent of *high dielectric constant* which is chemically indifferent to free electrons. The known examples would appear to be ammonia, organic amines, and possibly fused alkali metal amides.

¹ Richard A. Ogg, Jr., J. Am. Chem. Soc. **68**, 155 (1946). J. Chem. Phys. **14**, 114, 295 (1946). Phys. Rev. **69**, 243 (1946). Original literature references to earlier experimental work are given in these communications.

² C. A. Kraus, *The Properties of Electrically Conducting Systems* (Chemical Catalogue Company, 1922).

³ For fuller mathematical details, see G. Gamow, *Atomic Nuclei and Radioactivity* (Oxford University Press, New York, 1931), pp. 42-49.

⁴ L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), Appendix V.

Frequency Modulated Cyclotron

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THE application of the synchrotron phase stability principle^{1,2} to the frequency modulated cyclotron has been investigated experimentally on the 37-inch Berkeley cyclotron. A radial decrease in magnetic field has been used such that it requires a frequency change simulating the change which would be required by the relativistic increase of mass with velocity as the ions are accelerated to high speeds.

The frequency of revolution of an ion of kinetic energy W (units Mc²) in a magnetic field H is

$$f = \frac{f_c}{1 + W/H_c} H$$

where f_c is the frequency the ion would have with very low energy in the field H_c . Thus the change in frequency produced by an increase in W to a large value can be simulated by the proper radial decrease in magnetic field even though ions of a comparatively low energy are used. The purpose of the experiments described here was to simulate the acceleration of deuterons to 200 Mev in the giant 184-inch cyclotron. Here $W=0.107$ so that a total frequency change of 13 percent would leave 2.3 percent for radial decrease of magnetic field in the 184-inch case.

We have succeeded in accelerating a time average deuteron current of 0.2 microampere through a radial fall in magnetic field of 13 percent. This was accomplished by a radio frequency peak potential of 3 kv on the dee which accelerated the deuterons to 7 Mev. Without frequency modulation the maximum energy obtainable is 0.5 Mev with this voltage on the dee (in accord with theory). So far our maximum modulation frequency has been 600 cycles per second which corresponds to an acceleration