Bound States in a Debye-Hückel Potential

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This is a study of some of the properties of the discrete energy levels of an electron in an exponentially shielded Coulomb potential, which is known in plasma physics as the Debye-Hückel potential and in nuclear physics as the Yukawa potential. A system with this potential possesses a finite number of bound states and these states are not degenerate with respect to the orbital angular momentum. First-order perturbation theory is used to obtain simple, analytical expressions for estimating the energy levels; the approximations appear to be quite accurate for large values of the Debye length. The perturbation calculations lead to an estimate of the number of bound states as a function of the Debye length. The matrix elements of the Hamiltonian for this potential are calculated in the representation of the hydrogen atom wave functions. The Hamiltonian matrix may serve as a convenient starting point for several other methods of computing the energy levels.

1. INTRODUCTION

ALTHOUGH the two-component gas with Coulomb interactions has not yet been adequately treated, certain results are available for various temperature and density regions. Specifically, the Debye-Hückel potential is reported to be the effective two-body interaction in the high-temperature, low-density region.[1] This result is often interpreted to mean that in a hydrogen plasma a bound electron moves in the potential given by the Debye-Hückel theory. By virtue of their spectra, atoms in a plasma serve as noninterfering probes, and a study of the effects of the Debye shielding on the energy levels of atomic hydrogen may be of more than academic value. For example, in the highly excited bound states of atoms in a plasma the Debye shielding may be approximately realized, and one wishes to examine the effects of this shielding on the atomic partition function.

It is the purpose of the present paper to estimate the energy levels of an electron in a Debye-Hückel potential (which, in nuclear physics, is known as the Yukawa potential). Although certain aspects of the problem have been investigated by others,[2-5] it is not apparent that the problem has been treated as generally as might be desired. Ecker and Weizel[2] restrict their study to *s* states and their method of calculation is open to question.[6] Harris[3] has used a variational technique for making numerical estimations of several energy levels, but it appears that her results are not useful for laboratory plasmas, since she chooses mostly small values for the Debye length. Her energy levels for the larger Debye lengths are in agreement with those calculated from analytical expressions obtained in the present paper.

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2. PERTURBATION CALCULATIONS

The Debye (or Debye-Hückel) potential for an electron in the shielded field of a singly-charged ion is

$$V(r) = -\epsilon^2 (e^{-r/d}/r). \qquad (1)$$

Here ϵ is the unit of charge and d is the Debye length.

$$d = (kT/4\pi\epsilon^2 n)^{1/2}, \qquad (2)$$

where k is the Boltzmann constant, T is the equilibrium temperature of the plasma, and n is the electron density. The potential in Eq. (1) possesses a finite number of energy levels, and these energy levels are not degenerate with respect to the angular momentum.

Atomic units are employed, so that the unit of distance is $\hbar^2/\mu\epsilon^2$ and the unit of energy is $-\mu\epsilon^4/2\hbar^2$, where μ is the reduced mass of the electron. Instead of the radial wave function $R(r)$, it is desirable to use $P(r) \equiv rR(r)$ so that the radial Schrödinger equation with the potential of Eq. (1) becomes

$$\frac{d^2P}{dr^2} + \left(\frac{2e^{-r/d}}{r} - W\right)P - \frac{l(l+1)}{r^2}P = 0, \qquad (3)$$

where l is the angular-momentum quantum number and W is the negative of the energy eigenvalue of the electron. Note that $W \geq 0$ for bound states. The Debye length for a hydrogen plasma is usually larger than 10^{-6} cm, which, in terms of atomic units, means $d \geq 10^3$.

The potential in Eq. (1) may be written as a Coulomb potential plus a perturbation $U(r)$:

$$V(r) = 2/r + U(r) = 2/r + 2((e^{-r/d}-1)/r). \qquad (4)$$

It is seen that the perturbing potential $U(r)$ becomes comparable to $V(r)$ when $r \sim d$. For the unperturbed case the average value, $\langle r \rangle$, of r goes as N^2, where N is the principal quantum number. Thus, it is expected that first-order perturbation theory will be accurate as long as $N^2 \ll d$ and becomes progressively less accurate as N^2 approaches d. It is to be noted that the Debye potential is not meaningful for the lowest energy levels, since the electron orbits will not encompass

enough charged particles to realize any screening at all. Furthermore, for the lower states the orbital frequency of the electron may be large compared to the plasma frequency so that any static potential will be inapplicable to the problem.

The first-order energy shift ΔW_1 is given by

$$\Delta W_1 = (P_{Nl}, UP_{Nl}) \equiv \int_0^\infty [P_{Nl}(r)]^2 U(r) dr, \quad (5)$$

where the $P_{Nl}(r)$ are the normalized zero-order eigen-

functions of Eq. (3) and in this case are the radial hydrogen functions

$$P_{Nl}(r) = -\frac{1}{N}\left[\frac{(N-l-1)!}{[N+l)!]^3}\right]^{1/2}$$

$$\times e^{-r/N}\left(\frac{2r}{N}\right)^{l+1} L_{N+l}^{2l+1}\left(\frac{2r}{N}\right), \quad (6)$$

where $L_{N+l}^{2l+1}(2r/N)$ is the associated Laguerre polynomial. The integration in Eq. (5) may be performed and yields

$$\Delta W_1 = \frac{2^{2l+3}(N+l)!{}_2F_1(-N+l+1, -N+l+1, 2l+2, 4d^2/N^2)}{N^{2l+4}(2l+1)!(N-l-1)!(2/N+1/d)^{2N}d^{2N-2l-2}} - \frac{2}{N^2}, \quad (7)$$

where ${}_2F_1$ is the hypergeometric function.

If second and higher order terms in $1/d$ are neglected, Eq. (7) reduces to

$$\Delta W_1 \cong -2/(d+N^2). \quad (8)$$

Hence, to first order in $1/d$, first-order perturbation theory provides the following expression for the energy levels of Eq. (3):

$$W \cong 1/N^2 - 2/(d+N^2). \quad (9)$$

Although Eq. (9) indicates that energy levels of Eq. (3) are not degenerate with respect to the angular momentum, it is to be noted that the degeneracy still exists if second and higher order terms in $1/d$ are neglected.

A useful approximation to ΔW_1 is obtained by expanding $U(r)$ in a power series in $1/d$. If this is done Eq. (5) becomes

$$\Delta W_1 = -\frac{2}{d} + \frac{1}{d^2}\langle r \rangle - \frac{1}{3d^3}\langle r^2 \rangle + \frac{1}{12d^4}\langle r^3 \rangle - \frac{1}{60d^5}\langle r^4 \rangle + \cdots. \quad (10)$$

For $P_{Nl}(r)$ in the form given in Eq. (6) Bethe and Salpeter[7] have an explicit formula for evaluating $\langle r^\nu \rangle$ through $\nu=4$. Equation (10) then becomes[8]

$$\Delta W_1 \cong -\frac{2}{d} + \frac{1}{2d^2}[3N^2 - l(l+1)] - \frac{N^2}{6d^3}[5N^2 + 1 - 3l(l+1)]$$

$$+ \frac{N^2}{96d^4}[35N^2(N^2-1) - 30N^2(l+2)(l-1) + 3(l+2)(l+1)l(l-1)]$$

$$- \frac{N^4}{480d^5}[63N^4 - 35N^2(2l^2+2l-3) - 5l(l+1)(3l^2+3l-10)+12]. \quad (11)$$

Once the $l=0$ values are obtained for a given N, a useful approximation for ΔW_1 with higher l values is

$$\Delta W_1 = (P_{Nl}, UP_{Nl}) \cong (P_{N0}, UP_{N0})$$
$$- [l(l+1)/2d^3](d-N^2). \quad (12)$$

Again, it is noted from Eq. (12) that the angular momentum corrections are of order $1/d^2$ and higher.

Values of the perturbed eigenvalues W for a few values of N, l, and d are presented in Table I. The

calculations are based on Eq. (11). (The lower N values are included only for completeness.)

If accurate estimates of the eigenvalues of the Debye potential become necessary, an efficient method for computing the eigenvalues is the Rayleigh-Ritz method.[9] This method involves diagonalizing the Hamiltonian matrix computed in some convenient representation. Good accuracy of this method depends on a judicious choice of base vectors, which, in this case, should be the unperturbed eigenfunctions given by Eq. (6). The matrix for the Hamiltonian for a given l (H is central

[7] H. A. Bethe, and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), p. 17.

[8] H. W. Woolley (Ref. 5) obtained this expression through the d^{-4} term.

[9] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. I, Chap. 5.

TABLE I. Eigenvalues (W) as calculated
from perturbation theory.

d (a.u.)	N	$l=0$	$l=1$	$l=2$	Unperturbed
10^3	1	0.9980			1.0000
	2	0.2480	0.2480		0.2500
	3	0.1091	0.1091	0.1091	0.1111
	4	0.0605	0.0605	0.0605	0.0625
	5	0.0380	0.0380	0.0380	0.0400
	6	0.0258	0.0258	0.0258	0.0278
	7	0.0185	0.0185	0.0185	0.0204
	8	0.0137	0.0137	0.0137	0.0156
	9	0.0105	0.0105	0.0105	0.0123
	10	0.0081	0.0081	0.0081	0.0100
	11	0.0064	0.0064	0.0064	0.0083
	12	0.0051	0.0051	0.0051	0.0069
	13	0.0041	0.0041	0.0041	0.0059
10^2	1	0.9802			1.0000
	2	0.2306	0.2305		0.2500
	3	0.0924	0.0923	0.0921	0.1111
	4	0.0447	0.0446	0.0444	0.0625
	5	0.0233	0.0232	0.0230	0.0400

so that l values are not mixed) in this representation is

$$(P_{Nl}, HP_{N'l}) = (1/N^2)\delta_{NN'} + (P_{Nl}, UP_{N'l}), \quad (13)$$

where

$$(P_{Nl}, UP_{N'l}) \equiv \int_0^\infty P_{Nl} 2\left(\frac{e^{-r/d}-1}{r}\right) P_{N'l} dr. \quad (14)$$

With P_{Nl} given by Eq. (6) the matrix elements of $U(r)$, Eq. (14), become

$$A(N,N',l)\frac{\lambda_1^{\alpha+\alpha'-\gamma}}{(\lambda_1-k)^\alpha(\lambda_1-k')^{\alpha'}}$$

$$\times {}_2F_1\left(\alpha,\alpha',\gamma,\frac{kk'}{(\lambda_1-k)(\lambda_1-k')}\right)$$

$$-A(N,N',l)\frac{\lambda_2^{\alpha+\alpha'-\gamma}}{(\lambda_2-k)^\alpha(\lambda_2-k')^{\alpha'}}$$

$$\times {}_2F_1\left(\alpha,\alpha',\gamma,\frac{kk'}{(\lambda_2-k)(\lambda_2-k')}\right), \quad (15)$$

where

$$A(N,N',l) = \tfrac{1}{2}(2l+1)!\left(\frac{4}{NN'}\right)^{l+2}$$

$$\times\left[\frac{(N+l)!(N'+l)!}{(N-l-1)!(N'-l-1)!}\right]^{1/2},$$

$$\gamma = 2l+2, \qquad k = 2/N, \quad k' = 2/N',$$

$$\alpha = -N+l+1, \quad \lambda_1 = 1/N + 1/N' + 1/d,$$

$$\alpha' = -N'+l+1, \quad \lambda_2 = 1/N + 1/N'.$$

The evaluation of these matrix elements is rather tedious but could be rapidly executed on an electronic computer.

3. THE NUMBER OF ENERGY LEVELS FOR A DEBYE-HÜCKEL POTENTIAL

If Eq. (9) were exact, then the principal quantum number would satisfy the condition

$$N^2 \le d \quad (16)$$

since it is required that $W \ge 0$ for bound states. In spite of the limited accuracy of first-order perturbation theory and the approximation made in arriving at Eq. (8), the result in Eq. (16) compares favorably with results of others.[2,4] In fact, Eq. (16) is identical to an expression obtained by Ecker and Weizel.

In connection with a hydrogen plasma, such an expression as Eq. (16) is of limited usefulness, since other perturbations in the plasma must also be considered,[10] especially for $N^2 \sim d$. For example, if the l degeneracy is neglected, it is not to be assumed that $N = d^{1/2}$ energy levels must be included in the atomic partition function.

4. CONCLUDING REMARKS

The principal value of the results of this study is that several approximate expressions are made available, which reveal some of the interesting properties of the exponentially shielded Coulomb potential. It does not appear that these results alone have immediate application to the calculation of thermodynamic functions, since other large perturbative effects must also be superposed on the perfect gas behavior of a hydrogen plasma. At this point it is desirable to re-emphasize that the preceding calculations are relevant to plasmas only for large electron-protron separations and not for low-lying states. As already indicated, Eq. (16) should not be used in terminating the atomic partition function. In this connection it should be mentioned that the well-known work of Inglis and Teller,[10] which treats the effects of the interatomic Stark broadening, likewise should not be used in terminating the partition function. Their work is applicable only to estimating the number of distinct spectral lines emanating from a radiating gas: Even though the higher energy levels are Stark broadened to such an extent that the spectral lines coalesce into a continuum, these broadened levels still represent bound states and must be included in the atomic partition function. It is not at all clear how one should sum over such broadened levels.

[10] D. R. Inglis and E. Teller, Astrophys. J. 90, 439 (1939).