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Bound Eigenstates of the Exponential Cosine Screened Coulomb Potential*

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A number of properties of the bound eigenstates of an electron in an exponential cosine screened Coulomb potential, $V(r) = -(e^2/\kappa r)e^{-qr}\cos(qr)$, are studied. Perturbation and variation methods are used to calculate the eigenvalues. Detailed results are presented for the first four s states. For each state there is a critical value of the screening parameter δ_c above which no bound states with negative energy exist. The value of δ_c for the ground state is obtained from a two-parameter variational calculation. The total number of different energy levels is finite for any value of the screening parameter δ greater than zero, and is found to be approximately linearly dependent on $1/\delta_c$. The square of the number of bound s states is also shown to be linear with $1/\delta_c$. Positive-energy states are also discussed.

I. INTRODUCTION

The potential

$$V(r) = -\frac{e^2}{\kappa r}\, e^{-qr}\cos(qr)\,, \tag{1.1}$$

where κ is the dielectric constant and q is a screening parameter, is of importance in solid-state physics. Under certain conditions[1-5] it describes the potential between an ionized impurity and an electron in a metal. When $r \ll 1/k_0$, where $k_0 = (2m^*kT)^{1/2}/\hbar$ for the nondegenerate case and $k_0 = (3\pi^2 n)^{1/3}$ in the fully degenerate case, it represents the ionized impurity-electron potential in a semiconductor.[6,7] Prokop'ev[8] has used it to describe the electron-positron interaction in a positronium atom in a solid. We shall call this potential the exponential cosine screened Coulomb (ECSC) potential.

While a fair amount of work has been done on the properties of the well-known static screened Coulomb potential[9-11]

$$V(r) = -e^2 e^{-\alpha r}/r\,, \tag{1.2}$$

the ECSC potential has received scant attention. The only investigation on the bound states in this potential is that of Bonch-Bruevich and Glasko,[1,2] who have determined a few eigenvalues for the 1s state in the high-screening region by a numerical method and have also obtained the critical screening parameter.

The Schrödinger equation for the ECSC potential is not solvable analytically. In the present paper we have employed perturbation and variation methods to obtain the energy eigenvalues, the critical screening parameter, and the number of bound states for the potential (1.1). In Sec. II we carry out a first-order perturbation treatment with the Coulomb potential as the unperturbed potential and obtain a general expression for the perturbation energy for any value of n and l. It is shown in Sec. III that for s states better results are obtained by taking the Hulthén potential as the unperturbed potential. Section IV is devoted to a calculation of the eigenvalues by the variation method; the critical screening parameter is also obtained. Section V deals with the number of bound states and a comparison of the results.

Throughout this paper we use atomic units, where the unit of length is $a_0 = k\hbar^2/m^*e^2$ and the unit of energy is equal to $-m^*e^4/\kappa^2\hbar^2$. Here m^* is the effective mass and $\delta = qa_0$. In these units the ECSC potential can be written as

$$V(r) = (1/r)e^{-\delta r}\cos\delta r\,. \tag{1.3}$$

II. PERTURBATION CALCULATION WITH COULOMB POTENTIAL AS UNPERTURBED POTENTIAL

As a first approximation, we take the Coulomb potential as the unperturbed potential. Then the perturbation $U(r)$ is given by

$$U(r) = \frac{e^{-\delta r}}{r}\cos\delta r - \frac{1}{r}\,. \tag{2.1}$$

The unperturbed wave function has the form[12]

$$\Psi_{nl}(r)=\frac{2^{l+1}}{n^{l+2}}\left(\frac{(n+l)!}{(n-l-1)!}\right)^{1/2}\frac{1}{(2l+1)!}\,e^{-(r/n)}r^{l+1}{}_1F_1\left(-n+l+1,\ 2l+2;\ \frac{2r}{n}\right), \tag{2.2}$$

where ${}_1F_1$ is the confluent hypergeometric function.

The first-order energy shift is

$$\begin{aligned}\Delta E_{nl}&=\langle\Psi_{nl}(r)\,|\,U(r)\,|\,\Psi_{nl}(r)\rangle\\&=\frac{2^{2l+2}}{n^{2l+4}}\frac{(n+l)!}{(n-l-1)!}\frac{1}{(2l+1)!}\frac{\delta^{2n-2l-2}}{[(4/n^2)+(4\delta/n)+2\delta^2]^{2n}}\operatorname{Re}\left[(1-i)^{2n-2l-2}\left(\frac{2}{n}+\delta+i\delta\right)^{2n}\right.\\&\qquad\left.\times{}_2F_1\left(-n+l+1,\ \ -n+l+1;\ 2l+2;\ \frac{2i}{n^2\delta^2}\right)\right]-\frac{1}{n^2},\end{aligned} \tag{2.3}$$

where ${}_2F_1$ is the hypergeometric function.

The calculated values of energies for the $1s$, $2s$, $3s$, and $4s$ states, obtained on an IBM 360/65 in "double precision," are shown in Tables I–IV. Results for some further states are presented and discussed in Sec. V.

III. PERTURBATION CALCULATION WITH HULTHÉN POTENTIAL AS UNPERTURBED POTENTIAL

For small values of δr the behavior of the Hulthén potential[13]

$$V(r)=\frac{\delta e^{-\delta r}}{1-e^{-\delta r}} \tag{3.1}$$

is quite similar to that of the ECSC potential, and in this section we shall use the Hulthén potential as the unperturbed potential. The Schrödinger equation is analytically solvable for the potential (3.1) for $l=0$. The eigenvalue is given by[11]

$$E=\tfrac{1}{2}a_n^2\delta^2, \tag{3.2}$$

where $a_n=\frac{1}{2}(2/n\delta-n)$ and the normalized eigenfunction is

$$\begin{aligned}\Psi_n(r)&=\left(\frac{\delta(\beta_n-1)(\beta_n+2n-1)}{2(\beta_n+n-1)}\right)^{1/2}e^{-a_n\delta r}\\&\quad\times\sum_{\nu=1}^{n}(-1)^{\nu-1}\binom{n-1}{\nu-1}\binom{n+\beta_n+\nu-2}{\nu}(1-e^{-\delta r})^{\nu},\end{aligned} \tag{3.3}$$

where $\beta_n=(2/n\delta)-n+1$. In Fig. 1 we show the ECSC, Hulthén, and Coulomb potentials. It will be noticed that the choice of the Hulthén potential as the unperturbed potential is a better one than that of a Coulomb potential for the same.

The perturbation $U(r)$ can be then written as

$$U(r)=\frac{1}{r}\,e^{-\delta r}\cos\delta r-\frac{\delta e^{-\delta r}}{1-e^{-\delta r}}\,. \tag{3.4}$$

The final results, obtained through some lengthy calculations, from this perturbation calculation for the energies of the $1s$, $2s$, $3s$, and $4s$ states are given below:

TABLE I. Energy eigenvalues as a function of screening parameter for the $1s$ state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one parameter)	Variational (two parameter)
0.0001	0.499 900	0.499 900	...	
0.0002	0.499 800	0.499 800	0.499 800	
0.0005	0.499 500	0.499 500	0.499 500	
0.0010	0.499 000	0.499 000	0.499 000	
0.0020	0.498 000	0.498 000	0.498 000	
0.0050	0.495 000	0.495 000	0.495 000	
0.010	0.490 001	0.490 001	0.490 001	
0.020	0.480 008	0.480 008	0.480 008	
0.040	0.460 061	0.460 061	0.460 061	
0.060	0.440 200	0.440 201	0.440 201	
0.080	0.420 463	0.420 464	0.420 464	
0.10	0.400 883	0.400 884	0.400 885	0.400 885
0.20	0.306 235	0.306 298	0.306 332	0.306 334
0.30	0.218 619	0.219 028	0.219 399	0.219 411
0.40	0.139 153	0.140 595	0.142 375	0.142 418
0.50	0.068 047	0.071 714	0.077 481	0.077 606
0.60	0.004 987	0.012 585	0.027 708	0.028 031
0.70	−0.050 624	−0.036 908	0.000 184	0.000 614

$$E_{1s}=-\tfrac{1}{8}(4-\delta^2)+\frac{4-\delta^2}{2\delta^2}[-\ln(\delta^2+4)+2\ln(2\delta^2+4\delta+4)-\ln(5\delta^2+8\delta+4)], \qquad (3.5)$$

$$\begin{aligned}E_{2s}=-\tfrac{1}{8}(1-4\delta^2)+\frac{1-4\delta^2}{16\delta^4}[&-(1-\delta)^2\ln(2\delta^2-2\delta+1)+4(1-\delta)\ln(\delta^2+1)-2(3-\delta^2)\ln(2\delta^2+2\delta+1)\\&+4(1+\delta)\ln(5\delta^2+4\delta+1)-(1+\delta)^2\ln(10\delta^2+6\delta+1)] \quad (\delta\leq 1), \qquad 3.6)\end{aligned}$$

$$\begin{aligned}E_{3s}=-\tfrac{1}{72}(4-81\delta^2)+\frac{4-81\delta^2}{39366\delta^6}[&-(1-3\delta)^2(2-3\delta)^2\ln(45\delta^2-24\delta+4)+6(1-3\delta)(2-3\delta)^2\ln(18\delta^2-12\delta+4)\\&-3(2-3\delta)(10-15\delta-18\delta^2)\ln(9\delta^2+4)+2(4-9\delta^2)(2-9\delta^2)\ln(18\delta^2+12\delta+4)-3(2+3\delta)(10+15\delta-18\delta^2)\\&\times\ln(45\delta^2+24\delta+4)+6(1+3\delta)(2+3\delta)^2\ln(90\delta^2+36\delta+4)(1+3\delta)^2(2+3\delta)^2\ln(153\delta^2+48\delta+4)] \quad (\delta\leq\tfrac{1}{3}),\end{aligned}$$

$$(3.7)$$

$$\begin{aligned}E_{4s}=-\tfrac{1}{32}(1-64\delta^2)+\frac{1-64\delta^2}{1179648\delta^8}[&-(1-2\delta)^2(1-4\delta)^2(1-6\delta)^2\ln(40\delta^2-12\delta+1)\\&+8(1-2\delta)^2(1-4\delta)^2(1-6\delta)\ln(20\delta^2-8\delta+1)-4(1-2\delta)^2(1-4\delta)(7-28\delta-36\delta^2)\ln(8\delta^2-4\delta+1)\\&+8(1-4\delta)(1-4\delta^2)(7-14\delta-24\delta^2)\ln(4\delta^2+1)-2(1-4\delta^2)(35-380\delta^2+576\delta^4)\ln(8\delta^2+4\delta+1)\\&+8(1+4\delta)(1-4\delta^2)(7+14\delta-24\delta^2)\ln(20\delta^2+8\delta+1)-4(1+2\delta)^2(1+4\delta)(7+28\delta-36\delta^2)\ln(40\delta^2+12\delta+1)\\&+8(1+2\delta)^2(1+4\delta)^2(1+6\delta)\ln(68\delta^2+16\delta+1)-(1+2\delta)^2(1+4\delta)^2(1+6\delta)^2\ln(104\delta^2+20\delta+1)] \quad (\delta\leq\tfrac{1}{6}).\end{aligned}$$

$$(3.8)$$

The calculated energy values from the above expressions are shown in Tables I–IV. Though here we have obtained results only for the first four s states, the method is quite general and can be applied to any s state. The complexity of algebra, however, increases with the value of n. We may also note here that when δ is small there are large cancellations between the terms occurring in Eqs. (3.5)–(3.8), and a 16-significant-figure accuracy is not adequate. Most of the recorded results were obtained on an IBM 360/85 in "quadruple precision" (32-figure accuracy).

IV. VARIATIONAL CALCULATION

The similarity in the behavior of the ECSC and the Hulthén potentials for small values of δr suggested that it would be appropriate to employ Hulthén-type wave functions for a variational calculation. First we consider the results by a one-variational-parameter calculation. The trial functions chosen were of the form (3.3) with μ, a variational parameter, replacing δ. For instance, the $1s$ wave function is given by

$$\Psi_{1s}=[(4/\mu^2)-1]^{1/2}(e^{-(1-\mu/2)r}-e^{-(1+\mu/2)r}). \qquad (4.1)$$

The expressions for the energies of the $1s$, $2s$, $3s$, and $4s$ states are

$$E_{1s}=\frac{1}{2\mu^2}(4-\mu^2)\left(-\frac{\mu^2}{4}-\ln[\delta^2+(2+\delta-\mu)^2]+2\ln[\delta^2+(2+\delta)^2]-\ln[\delta^2+(2+\delta+\mu)^2]\right) \quad (\mu<2+\delta), \qquad (4.2)$$

$$\begin{aligned}E_{2s}=\frac{1}{16\mu^4}(1-4\mu^2)\{&-2\mu^4-(1-\mu)^2\ln[\delta^2+(1+\delta-2\mu)^2]+4(1-\mu)\ln[\delta^2+(1+\delta-\mu)^2]\\&-2(3-\mu^2)\ln[\delta^2+(1+\delta)^2]+4(1+\mu)\ln[\delta^2+(1+\delta+\mu)^2]\\&-(1+\mu)^2\ln[\delta^2+(1+\delta+2\mu)^2]\} \quad (2\mu<1+\delta), \qquad (4.3)\end{aligned}$$

$$\begin{aligned}E_{3s}=\frac{1}{39366\mu^6}(4-81\mu^2)\Big\{&-\frac{2187}{4}\mu^6-(1-3\mu)^2(2-3\mu)^2\ln[9\delta^2+(2+3\delta-9\mu)^2]\\&+6(1-3\mu)(2-3\mu)^2\ln[9\delta^2+(2+3\delta-6\mu)^2]-3(2-3\mu)(10-15\mu-18\mu^2)\ln[9\delta^2+(2+3\delta-3\mu)^2]\\&+2(4-9\mu^2)(10-9\mu^2)\ln[9\delta^2+(2+3\delta)^2]-3(2+3\mu)(10+15\mu-18\mu^2)\ln[9\delta^2+(2+3\delta+3\mu)^2]\end{aligned}$$

$$+6(1+3\mu)(2+3\mu)^2\ln[9\delta^2+(2+3\delta+6\mu)^2]-(1+3\mu)^2(2+3\mu)^2\ln[9\delta^2+(2+3\delta+9\mu)^2]\Big\}\quad (9\mu<2+3\delta),\qquad (4.4)$$

$$E_{4s}=\frac{1}{1179648\mu^8}(1-64\mu^2)\{-36864\mu^8-(1-2\mu)^2(1-4\mu)^2(1-6\mu)^2\ln[4\delta^2+(1+2\delta-8\mu)^2]$$
$$+8(1-2\mu)^2(1-4\mu)^2(1-6\mu)\ln[4\delta^2+(1+2\delta-6\mu)^2]-4(1-2\mu)^2(1-4\mu)(7-28\mu-36\mu^2)\ln[4\delta^2+(1+2\delta-4\mu)^2]$$
$$+8(1-4\mu)(1-4\mu^2)(7-14\mu-24\mu^2)\ln[4\delta^2+(1+2\delta-2\mu)^2]-2(1-4\mu^2)(35-380\mu^2+576\mu^4)\ln[4\delta^2+(1+2\delta)^2]$$
$$+8(1+4\mu)(1-4\mu^2)(7+14\mu-24\mu^2)\ln[4\delta^2+(1+2\delta+2\mu)^2]$$
$$-4(1+2\mu)^2(1+4\mu)(7+28\mu-36\mu^2)\ln[4\delta^2+(1+2\delta+4\mu)^2]+8(1+2\mu)^2(1+4\mu)^2(1+6\mu)\ln[4\delta^2+(1+2\delta+6\mu)^2]$$
$$-(1+2\mu)^2(1+4\mu)^2(1+6\mu)^2\ln[4\delta^2+(1+2\delta+8\mu)^2]\}\quad (8\mu<1+2\delta).\qquad (4.5)$$

The energies of these four states were obtained by minimizing each with respect to μ separately. The values of μ thus obtained are shown in Table V, and the corresponding energies are shown in Tables I–IV. The calculations were carried out on an IBM 360/85 in "quadruple precision"; however, even this accuracy was not enough for $\delta = 0.0001$, for which satisfactory results could not be obtained and are not shown. We may note here that the wave functions for the 2*s*, 3*s*, and 4*s* states with the given values of μ are not exactly orthogonal to the eigenfunctions of the corresponding lower states, but they are close to it, except when δ is large.

An important quantity for a screened potential is the critical screening parameter[9,10] at which the binding energy of an electron in that potential becomes equal to zero. In order to more precisely determine the critical screening parameter δ_c, we have carried out a calculation with a two-parameter variational trial function for the ground state, which has the form[13–16]

$$\Psi_{1s}(r)=\left[\lambda\left(\frac{4\lambda^2}{\mu^2}-1\right)\right]^{1/2}\left(e^{-[\lambda-(\mu/2)]r}-e^{-[\lambda+(\mu/2)]r}\right).\qquad (4.6)$$

For this wave function we derive

$$E_{1s}=-\frac{\mu^2}{8}\left(\frac{4\lambda^2}{\mu^2}-1\right)+\frac{\lambda}{2}\left(\frac{4\lambda^2}{\mu^2}-1\right)\{-\ln[\delta^2+(\delta+2\lambda-\mu)^2]+2\ln[\delta^2+(\delta+2\lambda)^2]-\ln[\delta^2+(\delta+2\lambda+\mu)^2]\}$$
$$(\mu-2\lambda<\delta).\qquad (4.7)$$

Up to six significant figures, the energies calculated from Eq. (4.7) do not show any difference from those obtained from the one-parameter wave function for $\delta < 0.1$, and these values are not shown. For $\delta > 0.1$, improved values were obtained. Values for $\delta \geqslant 0.1$ are presented in the last column of Ta-

TABLE II. Energy eigenvalues as a function of screening parameter for the 2*s* state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one parameter)
0.0001	0.124 900	0.124 900	
0.0002	0.124 800	0.124 800	0.124 800
0.0005	0.124 500	0.124 500	0.124 500
0.0010	0.124 000	0.124 000	0.124 000
0.0020	0.123 000	0.123 000	0.123 000
0.0050	0.120 002	0.120 002	0.120 002
0.010	0.115 013	0.115 013	0.115 013
0.020	0.105 104	0.105 104	0.105 104
0.040	0.085 765	0.085 768	0.085 769
0.060	0.067 385	0.067 408	0.067 421
0.080	0.050 222	0.050 310	0.050 384
0.10	0.034 425	0.034 668	0.034 935
0.20	−0.023 671	−0.019 323	

TABLE III. Energy eigenvalues as a function of screening parameter for the 3*s* state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one parameter)
0.0001	0.055 456	0.055 456	
0.0002	0.055 356	0.055 356	0.055 356
0.0005	0.055 056	0.055 056	0.055 056
0.0010	0.054 556	0.054 556	0.054 556
0.0020	0.053 556	0.053 556	0.053 556
0.0050	0.050 564	0.050 564	0.050 564
0.010	0.045 619	0.045 619	0.045 619
0.020	0.036 022	0.036 024	0.036 025
0.040	0.018 707	0.018 768	0.018 822
0.060	0.004 538	0.004 903	0.005 454

TABLE IV. Energy eigenvalues as a function of screening parameter for the 4s state.

Screening parameter δ	Perturbation (Coulomb)	Perturbation (Hulthén)	Variational (one parameter)
0.0001	0.031 150	0.031 150	
0.0002	0.031 050	0.031 050	0.031 050
0.0005	0.030 750	0.030 750	0.030 750
0.0010	0.030 250	0.030 250	0.030 250
0.0020	0.029 252	0.029 252	0.029 252
0.0050	0.026 275	0.026 275	0.026 275
0.010	0.021 436	0.021 437	0.021 437
0.020	0.012 539	0.012 557	0.012 572
0.040	−0.001 079	−0.000 670	0.000 118

ble I, and the corresponding optimized values of the parameters in Table VI.

To obtain the critical screening, two conditions must be satisfied:

$$E(\delta,\ \mu,\ \lambda)=0\ ; \qquad (4.8)$$

$$\frac{\partial E(\delta,\ \mu,\ \lambda)}{\partial\lambda}=0 \quad \text{or} \quad \frac{\partial E(\delta,\ \mu,\ \lambda)}{\partial\mu}=0\ . \qquad (4.9)$$

The first condition, in conjunction with Eq. (4.7), yields $\mu=2\lambda$. Setting $\mu=2\lambda$, minimization of E with respect to λ was carried out. Thus we obtained $\delta_c=0.7115$ at $\lambda=1.238$.

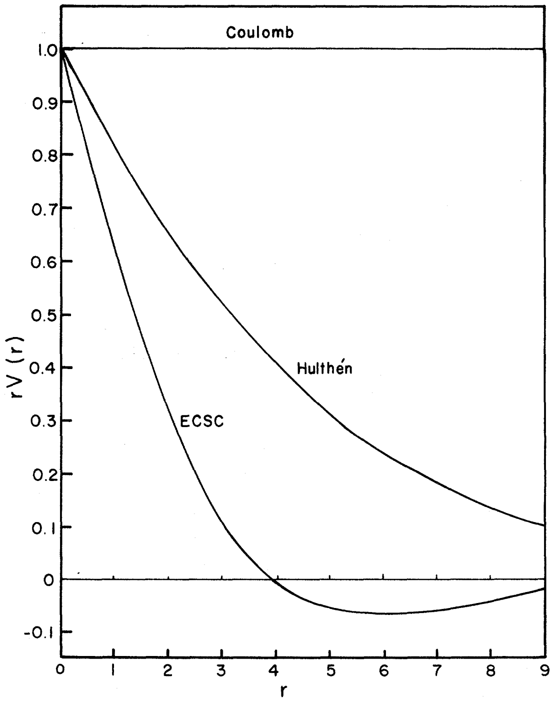

FIG. 1. Product $rV(r)$ as a function of r for the Coulomb potential, the Hulthén potential, and the ECSC potential, for $\delta=0.4$.

TABLE V. Best values of the parameter μ for the one-parameter-variational results.

Screening parameter δ	Parameter μ 1s	2s	3s	4s
0.0002	0.000 01	0.000 08	0.000 20	0.000 60
0.0005	0.000 04	0.000 10	0.000 30	0.000 62
0.0010	0.000 13	0.000 24	0.000 35	0.000 74
0.0020	0.000 37	0.000 68	0.000 98	0.001 28
0.0050	0.001 49	0.002 67	0.003 81	0.004 89
0.010	0.004 19	0.007 43	0.010 43	0.013 15
0.020	0.011 75	0.020 39	0.027 81	0.034 00
0.040	0.032 55	0.054 37	0.071 30	0.089 96
0.060	0.058 59	0.094 76	0.123 85	
0.080	0.088 41	0.139 43		
0.10	0.121 16	0.187 80		
0.20	0.313 48			
0.30	0.535 86			
0.40	0.781 41			
0.50	1.054 82			
0.60	1.376 79			
0.70	1.904 43			

V. NUMBER OF BOUND STATES AND COMPARISON OF RESULTS

We would like to note here that for the sake of brevity the results in Tables I–V are shown only for a few values of δ; more extensive tables have been deposited with NAPS.[17] The subsequent discussion takes cognizance of these extended results.

It will be noticed from Table I that for the ground state, for low values of δ (≤ 0.05), there is little difference between the three sets of results. However, as δ increases the accuracy of results improves in the following order: perturbation (Coulomb), perturbation (Hulthén), one-parameter variational calculation, two-parameter variational calculation. The last-named results are the most accurate.

The only other investigation with which we can compare our results is that of Bonch-Bruevich and Glasko,[1,2] who obtained their results by numerical methods. These authors have used a special set of units; when their results are converted into atomic units we find that in most cases their results are close to ours. For example, at $\delta=0.4793$, they get $E=0.0287$, while our two-parameter variational result is 0.028 77. At $\delta=0.5298$, their value is $E=0.0149$, compared to 0.014 96 obtained from Eq. (4.7). Bonch-Bruevich and Glasko's results lead to $\delta_c=0.72$, as compared to 0.7115 obtained in this paper.

The pattern of the results for the excited s states (Tables II–IV) is quite similar to that of the ground state. The Hulthén-perturbation results are better than the Coulomb-perturbation ones and the variational results are the best of the three.

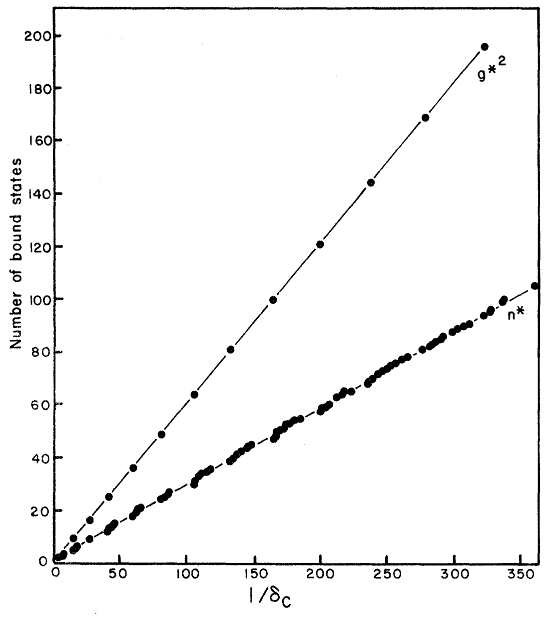

FIG. 2. Number of bound states n^* and the square of the maximum bound principal quantum number g^*, as a function of the critical screening length $1/\delta_c$.

For the static screened Coulomb potential (SSCP), a number of authors have investigated the number of bound states as a function of screening.[9,10,18-21] It is of interest to examine this relationship for the ECSC potential. The treatment given in Sec. II, while not yielding very accurate values, has the advantage that it can be used to obtain results for any state. We have calculated the energies and critical screening parameters of states up to $n = 15$ by this method. Some of the results for the energies are shown in Table VII. It will be noticed from this table that the excited states are not degenerate with respect to the orbital angular momentum. The number of bound states n^* was counted for various values of δ_c's. The results are shown in Fig. 2, where n^* is plotted vs $1/\delta_c$. A linear relationship is seen to hold between the two, and a least-squares fit yielded the following result:

$$n^* = 0.4425 + 0.2919/\delta_c \,. \tag{5.1}$$

Another quantity of interest is the "maximum-bound" principal quantum number g^*, or the number of bound s states. The quantity $(g^*)^2$ is also plotted against $1/\delta_c$ in Fig. 2, and is seen to exhibit a linear dependence on $1/\delta_c$. From a least-squares treatment we obtain

$$(g^*)^2 = 0.040 + 0.6078/\delta_c \,. \tag{5.2}$$

For a given value of δ, the perturbed-Coulomb-potential treatment gives binding energies which are too small. In other words, for a given value of δ, the number of bound states obtained from this method is smaller than the actual one. Thus the coefficients 0.2919 and 0.6078 in Eqs. (5.1) and (5.2), respectively, should be considered as a lower bound in the two cases. The intercepts at $1/\delta_c = 0$ are quite small in both cases, and within the accuracy of these results may be considered to be practically zero.

TABLE VI. Best values of parameters μ and λ for the 1s-state two-parameter wave function.

Screening parameter δ	Parameters μ	λ
0.10	0.180 36	1.002 41
0.20	0.357 29	1.004 58
0.25	0.473 31	1.007 29
0.30	0.595 16	1.010 58
0.40	0.867 49	1.021 48
0.50	1.177 00	1.039 19
0.60	1.571 50	1.076 10
0.70	2.260 80	1.188 11

The ECSC potential differs from the SSCP by the cosine factor. This factor leads to an oscillatory behavior of the ECSC potential. It is of obvious interest to compare the results for the ECSC potential with those for the SSCP. Generally speaking, the binding of the electron is weaker in the ECSC

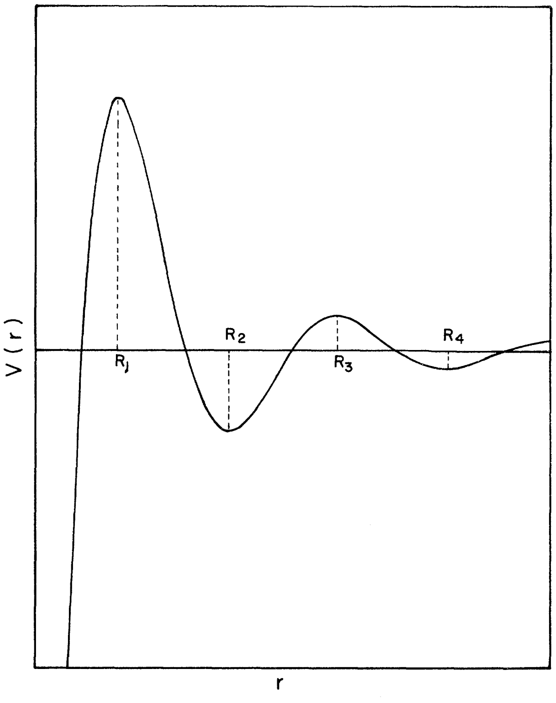

FIG. 3. Schematic diagram of the behavior of the ECSC potential as a function of r. As an aid to the eye, the relative strengths of oscillations have been exaggerated, for example, in reality $|V(R_2)/V(R_1)| \simeq 0.02$ rather than what is shown in the diagram.

TABLE VII. Energy eigenvalues as a function of screening parameter for the 2*p*, 3*p*, 3*d*, 4*p*, 4*d*, 4*f*, and 5*s*–8*k* states. δ_c values are also shown in the last column. The accuracy of the given values diminishes as δ/δ_c increases. Some estimate of the accuracy may be obtained by noting that at $\delta/\delta_c=\frac{1}{4}$ the accuracy is $\sim 0.005\%$ and at $\delta/\delta_c=\frac{1}{2}$ $\sim 0.5\%$. However, the relative accuracy of energies for levels having the same principal quantum number is much better, and for this reason a greater number of significant figures has been retained than is warranted by the absolute accuracy of the method.

state δ	0.000 1	0.000 2	0.000 5	0.001 0	0.002 0	0.005 0	0.010 0	0.020 0	0.050 0	0.100 0	δ_c
2*p*	0.124 900	0.124 800	0.124 500	0.124 000	0.123 000	0.120 001	0.115 010	0.105 075	0.076 049	0.032 042	0.143
3*p*	0.055 456	0.055 356	0.055 056	0.054 556	0.053 556	0.050 563	0.045 611	0.035 965	0.010 588		0.066
3*d*	0.055 456	0.055 356	0.055 056	0.054 556	0.053 556	0.050 561	0.045 595	0.035 849	0.009 292		0.062
4*p*	0.031 150	0.031 050	0.030 750	0.030 250	0.029 252	0.026 273	0.021 424	0.012 454			0.037
4*d*	0.031 150	0.031 050	0.030 750	0.030 250	0.029 251	0.026 270	0.021 397	0.012 283			0.036
4*f*	0.031 150	0.031 050	0.030 750	0.030 250	0.029 251	0.026 264	0.021 357	0.012 019			0.035
5*s*	0.019 900	0.019 800	0.019 500	0.019 001	0.018 004	0.015 059	0.010 419	0.002 663			0.024
5*p*	0.019 900	0.019 800	0.019 500	0.019 000	0.018 004	0.015 056	0.010 401	0.002 559			0.024
5*d*	0.019 900	0.019 800	0.019 500	0.019 000	0.018 003	0.015 051	0.010 364	0.002 350			0.024
5*f*	0.019 900	0.019 800	0.019 500	0.019 000	0.018 003	0.015 043	0.010 309	0.002 028			0.023
5*g*	0.019 900	0.019 800	0.019 500	0.019 000	0.018 002	0.015 032	0.010 233	0.001 583			0.022
6*s*	0.013 789	0.013 689	0.013 389	0.012 890	0.011 897	0.009 004	0.004 673				0.017
6*p*	0.013 789	0.013 689	0.013 389	0.012 890	0.011 897	0.009 001	0.004 651				0.017
6*d*	0.013 789	0.013 689	0.013 389	0.012 890	0.011 896	0.008 994	0.004 605				0.017
6*f*	0.013 789	0.013 689	0.013 389	0.012 890	0.011 895	0.008 983	0.004 537				0.016
6*g*	0.013 789	0.013 689	0.013 389	0.012 890	0.011 894	0.008 968	0.004 443				0.016
6*h*	0.013 789	0.013 689	0.013 389	0.012 889	0.011 893	0.008 950	0.004 324				0.015
7*s*	0.010 104	0.010 004	0.009 704	0.009 206	0.008 219	0.005 406	0.001 494				0.012
7*p*	0.010 104	0.010 004	0.009 704	0.009 206	0.008 218	0.005 401	0.001 468				0.012
7*d*	0.010 104	0.010 004	0.009 704	0.009 206	0.008 218	0.005 392	0.001 417				0.012
7*f*	0.010 104	0.010 004	0.009 704	0.009 206	0.008 217	0.005 379	0.001 339				0.012
7*g*	0.010 104	0.010 004	0.009 704	0.009 206	0.008 215	0.005 361	0.001 232				0.012
7*h*	0.010 104	0.010 004	0.009 704	0.009 205	0.008 214	0.005 337	0.001 096				0.011
7*i*	0.010 104	0.010 004	0.009 704	0.009 205	0.008 211	0.005 310	0.000 929				0.011
8*s*	0.007 713	0.007 613	0.007 313	0.006 816	0.005 837	0.003 134					0.0095
8*p*	0.007 713	0.007 613	0.007 313	0.006 816	0.005 837	0.003 128					0.0095
8*d*	0.007 713	0.007 613	0.007 313	0.006 816	0.005 836	0.003 118					0.0094
8*f*	0.007 713	0.007 613	0.007 313	0.006 815	0.005 834	0.003 102					0.0093
8*g*	0.007 713	0.007 613	0.007 313	0.006 815	0.005 833	0.003 080					0.0091
8*h*	0.007 713	0.007 613	0.007 313	0.006 815	0.005 830	0.003 053					0.0089
8*i*	0.007 713	0.007 613	0.007 313	0.006 814	0.005 828	0.003 020					0.0087
8*k*	0.007 713	0.007 613	0.007 313	0.006 814	0.005 825	0.002 981					0.0085

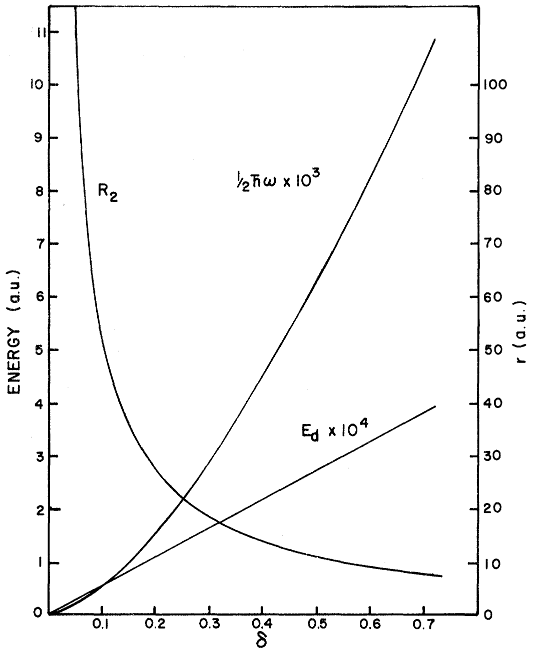

FIG. 4. Parameters of the first minimum: its position R_2, depth E_d, and the zero-point energy $\frac{1}{2}\hbar\omega$ as a function of δ.

potential than in the SSCP. There is a sharp reduction in the critical screening parameter δ_c: For the ECSC potential it is 0.7115, as compared to 1.19 for the SSCP.[10] For a given value of δ_c the quantities n^* and g^* for the ECSC potential are smaller than those for the SSCP.

Some Finer Points

The oscillating shape of the ECSC potential gives rise to some interesting properties which we now consider. In Fig. 3 we show the qualitative behavior of the ECSC potential; we shall find it convenient for our discussion. We wish to emphasize that it is only a qualitative diagram; in reality the amplitudes of the crests and troughs diminish much more rapidly than what is shown in the diagram. The positions of the maxima and minima can be obtained by putting the first derivative of Eq. (1.3) equal to zero, which leads to

$$1+(1/\delta R)+\tan\delta R=0\,. \qquad (5.3)$$

Equation (5.3) has, of course, multiple solutions; the first five of these are $\delta R = 2.1712$, 5.4134, 8.5844, 11.740, and 14.890. The potential barrier at R_1 can enable levels with positive energies to exist on its left side. The phenomenon is similar to that found in diatomic molecules where levels above the dissociation limit are known to exist for large values of the rotational quantum number, because of the potential hill created due to the rotational term $J(J+1)/r^2$. So far, in our case, we have considered only those bound levels which have negative energies with respect to the dissociation limit. We must now consider these positive-energy levels. In principle, a dissociation of the system can take place from these positive-energy states by tunneling through the potential hill, and this will also lead to a broadening of the discrete levels. However, these effects are expected to be important for only those levels which lie near the top of the potential hill. It is obvious that even for $\delta > \delta_c$ a given level can exist as a positive-energy level till its energy becomes equal to the height of the first maximum. This final value of δ beyond which no levels can exist (with negative or positive energies) will be denoted by δ_f. Our two-parameter variational wave function (4.6) is not satisfactory for obtaining positive-energy states and thus δ_f. However, by a graphical comparison of the two-parameter variational results with those from the Hulthén perturbation, we estimate $\delta_f \simeq 0.8$ for the ground state.

The ECSC potential has numerous minima (at R_2, R_4, ..., etc.) and if the depths of these wells are sufficiently large, metastable states can be formed in these. To obtain the precise location of these levels would require the application of some refined numerical techniques.[22] However, some order-of-magnitude estimates can be carried out by approximate means. The shape of these minima is similar to that of the potential-energy curve of a diatomic molecule in the neighborhood of its minimum, and it would be legitimate to estimate the position of the first level by calculating the zero-point energy from the second derivative of the potential. In this way we find that the zero-point energy at the first minimum is given by

$$\tfrac{1}{2}\hbar\omega=\delta^{3/2}\{4e^{-\delta R_2}(\delta R_2)^{-3}(\delta R_2+1)[\cos(\delta R_2)+\delta R_2\sin(\delta R_2)]\}^{1/2}\,. \qquad (5.4)$$

The depth of this well E_d is given by the energy difference between the first minimum and the second maximum:

$$E_d=\delta\left(\frac{e^{-\delta R_2}}{\delta R_2}\cos(\delta R_2)-\frac{e^{-\delta R_3}}{\delta R_3}\cos(\delta R_3)\right). \qquad (5.5)$$

In Fig. 4 we show some numerical results for the first minimum at R_2. It will be noticed from Eqs. (5.4) and (5.5) that the ratio $\frac{1}{2}\hbar\omega/E_d$ is a function of δ alone. We find from this ratio that $\frac{1}{2}\hbar\omega < E_d$ only when $\delta < 9.46\times10^{-4}$. Similarly for the second well at R_4, we find that $\frac{1}{2}\hbar\omega < E_d$ when $\delta < 9\times10^{-7}$. From these results it would be reasonable to infer that for $\delta > 1\times10^{-3}$ bound states do not exist in these wells. However, the possible existence of levels for $\delta < 1\times10^{-3}$ is a somewhat surprising conclusion from this analysis; it is possible that our method of estimating the zero-point energy in such shallow wells is not satisfactory. A definite conclusion on this point can only be obtained by a numerical integration of the Schrödinger equation for the ECSC potential.

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Electron Correlations and Quadrupole Hyperfine Structure of Li 2 ^2P†

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A perturbation calculation, based on restricted Hartree–Fock approximation, is carried out to second order in the residual interaction for the electric field gradient at the nucleus of Li 2 ^2P. It is shown that the second-order wave function is not required for the calculation of the second-order correction. We find that the second-order correction is nearly equal and opposite to the first-order (Sternheimer) correction.

I. INTRODUCTION

Atomic quadrupole hyperfine structure is caused by the interaction of the nuclear quadrupole moment with the electric field gradient at the nucleus due to the atomic electrons. Measurements of the hyperfine spectrum can be used to determine nuclear quadrupole moments by calculating expectation values of the electric field gradient.

A zeroth-order value of the field gradient q can be obtained from restricted Hartree–Fock (HF) theory. The first-order correlation correction to this (usually called the Sternheimer correction) is relatively easy to calculate and has been obtained for a large number of atomic states.[1] Recently two contributions have appeared in the literature which go beyond the Sternheimer correction for the $2P$ state of the lithium atom (for this state the Sternheimer correction is ~ -0.11 of the HF value). Calculations of correlation effects beyond the first order are difficult because they necessarily require a rather arbitrary choice of a finite set of functions to represent the Hilbert space. A perturbation calculation by Lyons *et al.*[2] evaluates the second-order correlation correction to the field gradient in addition to the first-order one. Nesbet[3] has carried out an elaborate variational calculation where single-particle and pair correlation effects are separately evaluated. An interesting aspect of these calculations is that they disagree on corrections beyond the Sternheimer term, not only in magnitude but also in sign. The calculation of Lyons *et al.* yields a second-order correction which enhances the value of the first-