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Variational wave functions for a screened Coulomb potential

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Using solutions to a Hulthèn-like effective potential as variational trail functions we have calculated the energy levels of the nonzero angular momentum states of the static screened Coulomb potential. Our one-parameter results for the $2p$, $3p$, $3d$, $4p$, $4d$, and $4f$ levels are in excellent agreement with earlier, more elaborate calculations. We have also calculated spontaneous emission transition probabilities between several pairs of states and find that our results compare favorably with previous calculations. We conclude that Hulthèn-like trial functions provide better variational energies and wave functions with fewer parameters than hydrogenic or Slater-type functions for screened Coulomb and similar potentials.

I. INTRODUCTION

The static screened Coulomb potential is a simple potential which has had great utility in a variety of fields such as solid-state, nuclear, and plasma physics. Several variational calculations[1-6] have been performed and tables of the energies as a function of the screening parameter have been compiled. One such study, that of Lam and Varshni,[5] showed that if one uses as trial functions eigenvectors of the Hulthèn potential rather than those of the simple Coulomb potential, excellent results for the energies of the s states of the screened Coulomb potential can be obtained with simple variational wave functions containing only one parameter. The method was limited to s states because the Schrödinger equation with a Hulthèn potential can be solved analytically only for states with zero angular momentum.

We present in this paper an extension of this method by using an "effective Hulthèn" potential for nonzero angular momentum which can be solved analytically. The resulting solutions when used as trial wave functions provide simple,one-parameter wave functions yielding energies for the $2p$, $3p$, $3d$, etc., states of the screened Coulomb potential of accuracy comparable to that of more elaborate studies.[4,6]

II. METHOD

The screened Coulomb potential is given in atomic units by

$$V_{\rm sc}(r) = -e^{-\delta r}/r\,. \tag{1}$$

Since it is a central potential, the Schrödinger equation can be separated into radial and angular parts in the usual way. The radial equation is given by

$$\left(-\frac{1}{2r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{e^{-\delta r}}{r} + \frac{l(l+1)}{2r^2}\right)R(r) = ER(r)\,.$$

If we write $\chi(r) = (1/r)R(r)$, this may be written as

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{e^{-\delta r}}{r} + \frac{l(l+1)}{2r^2}\right)\chi(r) = E\chi(r)\,. \tag{2}$$

The Hulthèn potential is defined as

$$V_H(r) = -\delta e^{-\delta r}/(1 - e^{-\delta r})\,. \tag{3}$$

It is easily seen that for small δ this potential closely approximates the screened Coulomb potential of Eq. (1). Moreover, as pointed out by Lam and Varshni,[5] $V_H(r)$ is a better approximation to $V_{\rm sc}(r)$ for all r than is the ordinary Coulomb potential; thus we would expect Hulthèn variational wave functions to give lower (and consequently better) energies for the screened Coulomb problem than the same number of Coulomb- (hydrogenic) type variational wave functions. This has been shown to be the case for the $1s$ to $4s$ states by Lam and Varshni.[5] Unfortunately, the radial Schrödinger equation for the Hulthèn potential can be solved analytically only for $l = 0$ states. Thus previous variational solutions for the nonzero angular momentum states have used hydrogenic functions or Slater-type orbitals for trial functions with three or more variational parameters necessary to obtain accurate energies.[3,6]

We have extended the Lam and Varshni approach by approximating the screened Coulomb effective potential,

$$V_{\rm sc}^{\rm eff}(r) = -e^{-\delta r}/r + l(l+1)/2r^2\,, \tag{4}$$

by what we will call the Hulthèn effective potential

$$V_H^{\rm eff}(r) = -\frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} + \frac{l(l+1)}{2}\left(\frac{\delta}{1 - e^{-\delta r}}\right)^2 e^{-\delta r}\,. \tag{5}$$

For small δr this effective potential approximates the screened Coulomb effective potential rather well, and in particular it gives the necessary repulsive core due to angular momentum. More importantly, the radial equation with (4) replaced by (5) can be solved analytically. The method of

TABLE I. Comparison of the screened Coulomb $2p$, $3p$, and $3d$ energy levels for several values of screening. All energies are in rydbergs.

Screening	$2p$		$3p$		$3d$	
δ	Present	Numerical [a]	Present	Numerical [a]	Present	Numerical [a]
0.001	−0.2480	−0.2480 [b]	−0.1091	−0.1091 [b]	−0.1091	−0.1091 [b]
0.010	−0.2305	−0.2305	−0.09231	−0.09231	−0.09212	−0.09212
0.020	−0.2119	−0.2119	−0.07570	−0.07570	−0.07503	−0.07503
0.025	−0.2030	−0.2030	−0.06816	−0.06816	−0.06715	−0.06715
0.050	−0.1615	−0.1615	−0.03711	−0.03712	−0.03383	−0.03383
0.100	−0.09307	−0.09307	−0.00317	−0.00318		
0.200	−0.00819	−0.00820				

[a] Rogers *et al.* (Ref. 4).
[b] Roussel and O'Connell (Ref. 6).

solution is the same as described by Lam and Varshni for s states, so we will only sketch the procedure here. We begin with the equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{\delta e^{-\delta r}}{1-e^{-\delta r}}+\frac{l(l+1)}{2}\left(\frac{\delta}{1-e^{-\delta r}}\right)^2 e^{-\delta r}\right]\chi'(r)=E'\chi'(r)\,, \quad (6)$$

where the primes indicate that the energy E' and wave function $\chi'(r)$ are not the solutions to the exact probelm, Eq. (2), but of the pseudoproblem given by Eq. (6). If we write

$$E'=-\tfrac{1}{2}\delta^2 a^2$$

and

$$\chi'(r)=e^{-a\delta r}\phi(r)\,,$$

we find that ϕ is the solution to the following equation:

$$-\frac{1}{2}\frac{d^2\phi}{dr^2}+a\delta\frac{d\phi}{dr}-\frac{\delta e^{-\delta r}}{1-e^{-\delta r}}\phi+\frac{l(l+1)}{2}\left(\frac{\delta}{1-e^{-\delta r}}\right)^2 e^{-\delta r}\phi=0\,.$$

A change of variables,

$$y=1-e^{-\delta r}\,,$$

then yields

$$y^2(1-y)\frac{d^2\phi}{dy^2}-(1+2a)y^2\frac{d\phi}{dy}+\frac{2}{\delta}y\phi-l(l+1)\phi=0. \quad (7)$$

If we now assume $\phi(y)$ to be of the form

$$\varphi(y)=\sum_{i=0}^{\infty}C_i y^{i+\sigma}\,, \quad (8)$$

and substitute it into Eq. (7), we find upon equating coefficients of like powers of y that $\sigma=l+1$ and that the C_i's satisfy the recursion relation

$$C_{i+1}=\frac{(i+l+1)(i+l)+(i+l+1)(1+2a)-2/\delta}{(i+l+1)(i+l+2)-l(l+1)}C_i\,. \quad (9)$$

Truncation of the series (8) after a finite number of terms (i.e., $C_{M+1}=0$) determines the quantity a_M, and hence the pseudoenergy E'_M from

$$(M+l+1)(M+l)+(M+l+1)(1+2a_M)-2/\delta=0$$

This will also provide the pseudo-wave-functions $\chi'_{Ml}(r)$. For example, with $l=1$, $M=0$ gives "$2p$" state; $M=1$ a "$3p$" state and so on. Setting $l=0$

TABLE II. Comparison of the screened Coulomb $4p$, $4d$, and $4f$ energy levels for several values of screening. All energies are in rydbergs.

Screening	$4p$		$4d$		$4f$	
δ	Present	Numerical [a]	Present	Numerical [a]	Present	Numerical [a]
0.001	−0.060 52	−0.060 52 [b]	−0.060 52	−0.060 52 [b]	−0.060 52	−0.060 52 [b]
0.005	−0.053 05	−0.053 05	−0.053 00	−0.053 01	−0.052 94	−0.052 94
0.010	−0.044 63	−0.044 63	−0.044 46	−0.044 45	−0.044 20	−0.044 20
0.020	−0.030 47	−0.030 47	−0.029 88	−0.029 88	−0.028 98	−0.028 98
0.025	−0.005 20	−0.005 20	−0.003 16	−0.003 16		

[a] Rogers *et al.* (Ref. 4).
[b] Roussel and O'Connell (Ref. 6).

will of course recover the usual Hulthèn solutions.

The functions

$$\chi'_{Ml}(r) = e^{-a_M\delta r} \sum_{i=0}^{\infty} C_i (1 - e^{-\delta r})^{i+l+1} \tag{10}$$

are not solutions to any real potential, but to the extent that the Hulthèn effective potential V_H^{eff} approximates $V_{\text{sc}}^{\text{eff}}$, they will approximate the screened Coulomb $\chi(r)$'s. This suggests that we use functions of the form of (10) with δ replaced by μ, a variational parameter, as trial functions in the variational solution of the screened Coulomb problem. We have done this for the $2p$, $3p$, $3d$, $4p$, $4d$, and $4f$ states and present our results in Sec. III.

III. RESULTS

If we assume that the radial trial functions $\chi'(r)$ are normalized; that is,

$$\int_0^\infty \chi'(r)^2 \, dr = 1 ,$$

then the variational energy is given by

$$\overline{E} = \int_0^\infty \chi'(r) \left(-\frac{1}{2} \frac{d^2}{dr^2} - \frac{e^{-\delta r}}{r} + \frac{l(l+1)}{2r^2} \right) \chi'(r) dr . \tag{11}$$

Minimizing this with respect to the variational parameter μ gives our best estimates of the energies of the screened Coulomb problem.

As a concrete example, let us consider the $2p$ case. For this case the trial radial function is

$$\begin{aligned} \chi'_{01}(r) &= \left(\frac{(1-4\mu^2)(1-\mu^2)}{24\mu^4} \right)^{1/2} e^{-(1/2\mu-1)\mu r} (1 - e^{-\mu r})^2 \\ &= \left(\frac{(1-4\mu^2)(1-\mu^2)}{24\mu^4} \right)^{1/2} e^{-r/2} (e^{\mu r/2} - e^{-\mu r/2})^2 . \end{aligned} \tag{12}$$

Using this in equation (11) we find

$$\begin{aligned} \overline{E}_{2p} = {} & [(1-\mu^2)(1-4\mu^2)/24\mu^4] \\ & \times [\mu^4/(1-\mu^2) + (1-2\mu)\ln(1-2\mu) - 4(1-\mu)\ln(1-\mu) - 4(1+\mu)\ln(1+\mu) + (1+2\mu)\ln(1+2\mu) \\ & + \ln(1+\delta-2\mu) - 4\ln(1+\delta-\mu) + 6\ln(1+\delta) - 4\ln(1+\delta+\mu) + \ln(1+\delta+2\mu)] . \end{aligned}$$

Minimization of this expression with respect to μ will give an upper bound to the screened Coulomb $2p$ energy for given value of the screening parameter δ. Note, however, that during this minimization we must require that $|\mu| < \frac{1}{2}$ in order that our wave function (12) go to zero for large r. There are similar conditions on the parameter μ for higher states.

Expression for the energies of other states can be obtained, but we will not give them here. For states other than those with one-term trial functions ($2p$, $3d$, $4f$, etc.) the energy is more easily calculated by computer using binomial expansions and analytic formulas for the required integral types. We present in Tables I and II results for the $2p$, $3p$, $3d$, $4p$, $4d$, and $4f$ states for several values of the screening parameter. Also given in the tables are the corresponding results of Rogers *et al.*[4] obtained from numerical integration of the differential equation. Roussel and O'Connell[6] obtained results virtually identical to those of Rogers *et al.*, so we have not included their results in the table. As can be seen, our one parameter results are very close to those of Rogers *et al.*

TABLE III. Best values of the variational parameter μ for the states of Tables I and II for several values of the screening parameter δ.

δ	$2p$	$3p$	$3d$	$4p$	$4d$	$4f$
0.001	0.0023	0.0023	0.0023	0.0023	0.0019	0.0023
0.010	0.0239	0.0233	0.0235	0.0226	0.0228	0.0230
0.020	0.0470	0.0450	0.0455	0.0427	0.0432	0.0440
0.025	0.0582	0.0552	0.0561	0.0518	0.0526	0.0539
0.050	0.1120	0.1027	0.1059	0.0926	0.0966	
0.100	0.2108	0.1849				
0.200	0.3967					

In Table III we list values of the variational parameter μ corresponding to the energies of Tables I and II. Since for given screening parameter δ the optimum values for the parameters μ vary from state to state, higher-level variational wave functions will not, without some modification, be orthogonal to lower states of the same symmetry (e.g., our $3p$ is not quite orthogonal to our $2p$). The energies of the higher states in Tables I and II and the μ values in Table III are for not-quite-orthogonal wave functions. (There is, of course, exact orthogonality between states of different angular momentum, due to the angular part of the wave functions.) Because of the excellent agreement with Rogers *et al.*[4] we did not expect that this nonorthogonality would seriously degrade our eigenvalues. To test this belief we repeated calculations of the energies of the $3p$ and $4d$ levels

TABLE IV. Comparison of spontaneous emission transition probabilities A_{ij} for several pairs of states.

Screening	$2p\rightarrow 1s$		$3p\rightarrow 1s$		$3d\rightarrow 2p$	
δ	Present	RO [a]	Present	RO [a]	Present	RO [a]
0.001	6.26	6.27	1.67	1.68	0.646	0.648
0.010	6.25	6.26	1.65	1.66	0.637	0.639
0.025	6.17	6.18	1.57	1.57	0.600	0.601
0.050	5.93	5.93	1.31	1.32	0.483	0.482
0.100	5.07	5.06	0.502	0.526		
0.200	2.20	2.16				

[a] Roussel and O'Connell (Ref. 6).

explicitly orthogonalizing the trial functions to the previously determined $2p$ and $3d$ levels before minimizing the variational energy. Our eigenvalues changed by less than 0.1% throughout the range δ. The largest difference in each case occurred for δ near the critical screening for which the energy of the state in question becomes zero.

We have also calculated the spontaneous emission transition probability[7]

$$A_{ij}=(4e^2/3\hbar c^3)\omega_{ij}^3\,|\langle i|\vec{r}\,|j\rangle|^2$$

for several pairs of states. These are presented in Table IV along with the corresponding values obtained by Roussel and O'Connell.[6] The required $1s$ Hulthèn-like wave function was taken from the paper of Lam and Varshni.[5] As with the energies presented earlier, the $3p$ wave function used is not orthogonal to our best $2p$ wave function. For small δ the agreement with Roussel and O'Connell is quite good. Near the critical screening for the higher state the agreement is less satisfactory. It appears that a linear combination of Hulthèn-like functions is necessary to provide accurate matrix elements near the critical screening.

IV. SUMMARY AND CONCLUSIONS

Using the solutions to a Hulthèn-like effective potential as one-parameter trial functions in a variational calculation of the screened Coulomb potential, we have calculated energy levels of the $2p$, $3p$, $3d$, $4p$, $4d$, and $4f$ states which are in excellent agreement with the more elaborate calculations of Rogers *et al.*[4] and Roussel and O'Connell.[6] Transition probabilities are also in good agreement with those given by the latter authors, leading us to believe that our simple wave functions can profitably be used to calculate other properties of screened Coulomb or similar short-range potentials when it is inconvenient or infeasible to use more involved variational or numerical wave functions. If greater accuracy is needed it appears that a linear combination of Hulthèn-like trial functions would be more suitable than a similar combination of hydrogenic or Slater-type functions.

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