

constant, so as to match the experimental dipole moments. Table III shows the results, and the striking result is that small changes in b , on the order of a few percent, leave the force constants largely unchanged, but alter the dipole moments by more than an order of magnitude.

The conclusion is therefore the following: While Phillips's model of diatomic molecules explains the binding forces and charge distributions in terms of a simple, physical picture, it does not seem to be possible to determine all three of the model parameters, b , Z_b , and q , from properties of the atoms alone. In his work on hydrides,

Phillips choose to take the values of q from CNDO calculations. I prescribed b , but my attempt to determine b in terms of the covalent radii can not be termed a success. If all I wanted was a model of diatomic molecules, this would not be too serious, but, of course, what I really want is a model which can also be applied to more complicated molecules, based on the data for diatomic molecules. And in view of the extreme sensitivity of the charge distribution to changes in b , it is almost certain that the appropriate value of b for a particular bond will not be the same in a diatomic molecule as in a large molecule.

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SO(2, 1) and the Hulthén Potential

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The s -state eigenfunctions of the Schrödinger equation for an electron in a Hulthén potential are shown to form a basis for an irreducible unitary representation of SO(2,1). The properties of this SO(2,1) are then applied to a study of the difference between the Hulthén potential and a screened Coulomb potential. Results compare well with those obtained by Lam and Varshni using a direct integration.

I. INTRODUCTION

Recently, a number of authors¹⁻⁹ have considered the use of group theory in problems involving integrals of radial operators. In traditional atomic physics, of course, group theory has been applied only to the angular wave function and this extension to studies of radial functions has necessitated the development of new techniques (new at least, for atomic physicists) and new viewpoints. As a result, work has been confined to studies of well-known quantum-mechanical systems: the nonrelativistic¹⁻⁵ and relativistic⁶ hydrogen atom, the generalized Kepler problem,⁶ and the harmonic oscillator.⁷⁻⁹ Although none of this work has yet led to applications involving more complicated atomic systems, each has contributed to a better

definition of techniques to be used and a better understanding of the problems remaining.

In this paper we wish to study, using group theory, the solution to the Schrödinger equation for an electron in a Hulthén potential¹⁰

$$V_H(r) = -e^2[\alpha e^{-\alpha r}/(1 - e^{-\alpha r})] \quad (1)$$

This potential is widely used in physics because the s -state solution for such a potential can be obtained in closed form. In addition to leading to a soluble Schrödinger equation, the Hulthén potential is a good approximation to the Yukawa-like potential

$$V_r(r) = -e^2(e^{-\alpha r}/r) \quad (2)$$

and is, therefore, a physically meaningful potential. As a result of these two characteristics,

the Hulthén potential has been used in a number of areas of physics ranging from nuclear physics¹¹ to scattering theory¹² to atomic physics.^{13,14} In atomic physics, the Hulthén wave function has been found to be very useful in variational problems¹³ where it may be used instead of, for example, a Slater function. Lam and Varshni¹⁴ have recently used the Hulthén potential and perturbation theory to calculate the energy eigenvalues for an electron in a screened Coulomb potential (Eq. 2).

In this paper, we will apply the group theory of Hulthén wave functions to the problem studied by Lam and Varshni.¹⁴ In keeping with the philosophy discussed in the first paragraph of this paper, the goal of this study is not to obtain new results specifically related to the problem studied by Lam and Varshni, but rather to further develop the application of group theory to radial functions.

II. SCHRÖDINGER EQUATION WITH HULTHÉN POTENTIAL

The Hulthén potential (Eq. 1) is, of course, central, which allows us to write the eigenfunction of the Schrödinger equation in the form $\psi_{nlm_l} = Y_{lm_l}(\theta, \varphi)R_{nl}(r)/r$. The Schrödinger equation itself can be split into separate angular and radial equations; the latter is given by

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{e^2 \alpha e^{-\alpha r}}{1 - e^{-\alpha r}} \right) R_{nl}(r) = E_{nl} R_{nl}(r). \quad (3)$$

We wish to consider solutions to this equation for $l=0$; Eq. (3) can then be rewritten in atomic units as

$$\left(\frac{1}{2} \frac{d^2}{dr^2} + \frac{\delta e^{-\delta r}}{1 - e^{-\delta r}} - \frac{a_n^2 \delta^2}{2} \right) R_{n0} = 0, \quad (4)$$

where r is measured in units of a_0 , E in units of $-me^4/\hbar^2$, $\delta = \alpha a_0$, and $a_n = (2E)^{1/2}/\delta$. It is convenient to change variables from r to $y = 1 - e^{-\delta r}$, in which case Eq. (4) becomes

$$\left(y^2(1-y) \frac{d^2}{dy^2} - y^2 \frac{d}{dy} + \frac{2y}{\delta} - a_n^2 \frac{y^2}{(1-y)} \right) R_{n0} = 0. \quad (5)$$

Solutions to this equation are well known.¹⁰ They are (normalized)

$$R_{n0} = \left(\frac{\delta(c_n - n)(c_n + n)}{2c_n} \right)^{1/2} (1-y)^{(c_n - n)/2} \times \sum_{\nu=1}^n (-1)^{\nu-1} \frac{(n-1)! \Gamma(c_n + \nu)}{(n-\nu)! (\nu-1)! \nu! \Gamma(c_n)} y^\nu, \quad (6)$$

where $c_n = 2/n\delta$. The corresponding eigenvalue is $E_n = \frac{1}{2} a_n^2 \delta^2$, where

$$a_n = \frac{1}{2} [2/(n\delta) - n] = \frac{1}{2} (c_n - n). \quad (7)$$

III. GROUP THEORY OF HULTHÉN POTENTIAL

We define the three operators

$$\begin{aligned} J_+ &= e^{it}(1-y)^{-1/2} \left(y(1-y) \frac{\partial}{\partial y} - \frac{cy}{2} - \frac{i}{2}(2-y) \frac{\partial}{\partial t} \right), \\ J_- &= e^{-it}(1-y)^{-1/2} \left(y(1-y) \frac{\partial}{\partial y} + \frac{cy}{2} + \frac{i}{2}(2-y) \frac{\partial}{\partial t} \right), \\ J_3 &= i \frac{\partial}{\partial t}. \end{aligned} \quad (8)$$

Direct calculation shows that these three operators form an algebra isomorphic to the complexification of the algebra of SO(2, 1):

$$[J_3, J_\pm] = \pm J_\pm, \quad [J_+, J_-] = 2J_3. \quad (9)$$

We next find a basis for a representation of this algebra on the space of functions y^k . In particular, we construct a representation for D_0^+ , the positive discrete unitary irreducible representation of SO(2, 1).¹⁵ The basis functions φ_n for this representation can be normalized such that they satisfy the equations

$$\begin{aligned} J_3 \varphi_n &= n \varphi_n, \\ J_\pm \varphi_n &= \pm [n(n \pm 1)]^{1/2} \varphi_{n \pm 1}, \end{aligned} \quad (10)$$

where n is a positive integer. Using Eqs. (8) and (10), one can construct an explicit form of the basis state φ_n ; we find

$$\begin{aligned} \varphi_n &= \left(\frac{cn}{2\pi} \right)^{1/2} e^{int} (1-y)^{(c-n)/2} \\ &\times \sum_{\nu=1}^n (-1)^{\nu-1} \frac{(n-1)! \Gamma(c+\nu)}{(n-\nu)! (\nu-1)! \Gamma(c+1) \nu!} y^\nu. \end{aligned} \quad (11)$$

The scalar product in this space can be defined as

$$(\varphi_n | \varphi_n) = \int_0^1 \int_0^{2\pi} \varphi_n^* \varphi_n d\Omega, \quad (12)$$

where $d\Omega = dt dy/y^2$. The functions φ_n are orthonormal with respect to this scalar product. In addition, we have

$$(J_\pm \varphi_n | \varphi_n) = -(\varphi_n | J_\mp \varphi_n) \quad (13)$$

and

$$(J_3 \varphi_n | \varphi_n) = (\varphi_n | J_3 \varphi_n).$$

Finally, we can write the Casimir operator for this SO(2, 1) algebra as

$$\begin{aligned} G &= J_+ J_- + J_3^2 - J_3 \\ &= y^2(1-y) \frac{\partial^2}{\partial y^2} - y^2 \frac{\partial}{\partial y} - icy \frac{\partial}{\partial t} \\ &\quad - \frac{y^2}{4(1-y)} \left(c + i \frac{\partial}{\partial t} \right)^2. \end{aligned} \quad (14)$$

Then, we must have $G\varphi_n = 0$.

When one makes the substitution $c = c_n$, one finds that

$$\varphi_n = e^{int} \left(\frac{c_n n^2}{2\pi(c_n - n)(c_n + n)} \right)^{1/2} R_{n0}, \quad (15)$$

and that $G\varphi_n$ is identical to Eq. (5). Of course, G is defined in terms of the operators of Eqs. (8), so in order to replace c by c_n in G , one must make the same replacements in Eqs. (8). However, it makes no sense to replace c by $c_n = 2/n\delta$ in Eqs. (8) since n is an eigenvalue of J_3 , i. e., a function of a particular basis state, and therefore should not appear in the definition of the operators. One can, of course, replace c by the operator $2/J_3\delta$, which will have an eigenvalue $2/n\delta$ thus removing this objection. This replacement leads to a further complication however, in that the operators of Eqs. (8) no longer form an algebra if one changes c to $2/J_3\delta$. Thus, we find that if we are to preserve our algebra, c in Eqs. (8) must be a constant $c \neq c(n)$. One is, therefore, led to the conclusion that if c is chosen such that Eq. (15) holds for a particular value of n , then the state $J_+\varphi_n (J_-\varphi_n)$ will not be proportional to the state $R_{n+10} (R_{n-10})$.

This difficulty is not unlike one which has already been noted in the group-theoretical studies of hydrogenic radial functions.²⁻⁵ In hydrogen, the radial variable is not r but r/n ; group-theoretical studies of the radial function have to be carried out in the space of a variable $z \neq z(n)$. This space coincides with the space of the hydrogenic functions at only one point. As a result, hydrogenic radial matrix elements diagonal in n are the only ones which have been evaluated using group theory.¹⁶ The same type constraint applies to the present problem: We must work in the space of constant c , i. e., we can consider only matrix elements diagonal in n .

IV. GROUP-THEORETICAL FORMULATION OF LAM-VARSHNI PROBLEM

Lam and Varshni¹⁴ obtained approximate eigenvalues for the screened Coulomb potential [Eq. (2)] by using the Hulthén potential [Eq. (1)] as a zeroth-order approximation, and evaluating the perturbation

$$\begin{aligned} U(r) &= V_Y(r) - V_H(r) \\ &= (e^{-6r}/r) - \delta e^{-6r}/(1 - e^{-6r}) \\ &= -[\delta(1-y)/y][1 + y/\ln(1-y)] \end{aligned} \quad (16)$$

in first order. Expressing the matrix element of the first-order perturbation in the notation of Sec. III, we find

$$\int_{R_{n0}^2} U(r) dr = \left(\frac{(c_n - n)(c_n + n)}{c_n n^2} \right) (\varphi_n | \bar{U}(y) | \varphi_n)_n, \quad (17)$$

where

$$\bar{U}(y) = \frac{U(r)y^2}{\delta(1-y)} = -y \left(1 + \frac{y}{\ln(1-y)} \right)$$

and the subscript n to the matrix element on the right indicates that it should be evaluated in the space of $c = c_n$.

In order to carry out the evaluation of the perturbation $U(r)$ using group theory, one needs to express $\bar{U}(y)$ on terms of "spherical tensors" in $SO(2,1)$. Spherical tensors are operators which transform according to certain representations of $SO(2,1)$. In our case, we are interested in operators $P_q^{(k)}$ which transform according to finite-dimensional nonunitary irreducible representations of the group.^{2,7} In particular, these operators are defined by the commutation relations

$$\begin{aligned} [J_\pm, P_q^{(k)}] &= [(k \mp q)(k \pm q + 1)]^{1/2} P_{q\pm 1}^{(k)}, \\ [J_3, P_q^{(k)}] &= q P_q^{(k)}, \end{aligned}$$

where $|q| \leq k$.

We need to obtain spherical tensors which can be expressed in terms of positive powers of y since $\bar{U}(y)$ can be expressed in these terms. In addition, we are interested only in operators $P_0^{(k)}$, since the selection rule^{2,7}

$$(\varphi_n | P_q^{(k)} | \varphi_n) = A(n, k) \delta(q, 0)$$

is rigorous. Such operators are easily found:

$$P_0^{(k)} = \sum_{\nu=0}^{\infty} \left(\frac{(k+\nu)!}{k!} \right)^2 \frac{(2k+1)!}{(2k+\nu+1)! \nu!} y^{k+1+\nu}. \quad (18)$$

The first few coefficients resulting from this expansion are given in Table I for $P_0^{(1)}$ through $P_0^{(5)}$.

One now expresses $\bar{U}(y)$ in terms of the $P_0^{(k)}$. Clearly an expansion of $\bar{U}(y)$ in terms of positive powers of y leads to an infinite series:

$$\begin{aligned} \bar{U}(y) &= -y[1 + y/\ln(1-y)] \\ &\approx -\left(\frac{1}{2}y^2 + \frac{1}{12}y^3 + \frac{1}{24}y^4 + \frac{19}{720}y^5 + \dots\right). \end{aligned} \quad (19)$$

In general, we can expect only the first few powers of y to be of importance because the wave functions themselves drop off rapidly with increasing y (y is, of course, always less than or equal to 1). Combining Eqs. (17) and (18), one obtains

TABLE I. The spherical tensors $P_0^{(k)}$ to order y^6 .

$P_0^{(1)} = y^2 + y^3 + \frac{9}{10}y^4 + \frac{4}{5}y^5 + \frac{5}{7}y^6 + \dots$
$P_0^{(2)} = y^3 + \frac{3}{2}y^4 + \frac{12}{7}y^5 + \frac{25}{14}y^6 + \dots$
$P_0^{(3)} = y^4 + 2y^5 + \frac{25}{9}y^6 + \dots$
$P_0^{(4)} = y^5 + \frac{5}{2}y^6 + \dots$
$P_0^{(5)} = y^6 + \dots$

TABLE II. The coefficients B_n^k .

$n \backslash k$	1	2	3	4
1	1	1	1	1
2	$\frac{1}{2}$	1	$\frac{7}{4}$	$\frac{11}{4}$
3	$\frac{1}{3}$	1	$\frac{23}{8}$	$\frac{17}{3}$
4	$\frac{1}{4}$	1	$\frac{27}{8}$	$\frac{39}{4}$

$$\bar{U}(y) = -\frac{1}{2}P_0^{(1)} + \frac{5}{12}P_0^{(2)} - \frac{13}{80}P_0^{(3)} + \dots \quad (20)$$

correct through order y^4 .

Matrix elements of $\bar{U}(y)$ can now be easily evaluated using the group properties of the states and the tensors. One can use the Wigner-Eckart theorem to write^{2,7}

$$\langle \varphi_n | P_0^{(k)} | \varphi_n \rangle = A(0n, k0 | 0n) \langle \varphi | P^{(k)} | \varphi \rangle, \quad (21)$$

where $A(\)$ is a Clebsch-Gordan coefficient for SO(2, 1) and $\langle \varphi | P^{(k)} | \varphi \rangle$ is a reduced matrix element which is independent of n . Then we have

$$\begin{aligned} \langle \varphi_n | P_0^{(k)} | \varphi_n \rangle &= \frac{A(0n, k0 | 0n)}{A(01, k0 | 01)} \langle \varphi_1 | P_0^{(k)} | \varphi_1 \rangle \\ &= (n-1)! \sum_t \frac{(k+t)!}{(n-t-1)!(t+1)!t!^2(k-t)!} \end{aligned} \quad (22a)$$

$$\times \langle \varphi_1 | P_0^{(k)} | \varphi_1 \rangle \quad (22b)$$

$$= n^2 B_n^k \langle \varphi_1 | P_0^{(k)} | \varphi_1 \rangle. \quad (22c)$$

In obtaining Eq. (22b) above, we have used the explicit form of the SO(2, 1) Clebsch-Gordan coefficient as obtained by Armstrong.^{2,7} The coefficient B_n^k is given in Table II for several values of k and n .

The matrix elements $\langle \varphi_1 | P_0^{(k)} | \varphi_1 \rangle$ are particularly easy to evaluate due to the simple form of φ_1 :

$$\varphi_1 = (c/2\pi)^{1/2} e^{it} (1-y)^{(c-1)/2} y.$$

Then we have

$$\begin{aligned} \langle \varphi_1 | P_0^{(1)} | \varphi_1 \rangle &= \frac{2(c^2 + 10c + 34.8)}{(c+4)(c+3)(c+2)(c+1)}, \\ \langle \varphi_1 | P_0^{(2)} | \varphi_1 \rangle &= \frac{6(c+10)}{(c+4)(c+3)(c+2)(c+1)}, \\ \langle \varphi_1 | P_0^{(3)} | \varphi_1 \rangle &= \frac{24}{(c+4)(c+3)(c+2)(c+1)} \end{aligned} \quad (23)$$

correct through order y^4 in the expansion of the $P_0^{(k)}$.

V. RESULTS AND DISCUSSION

The perturbation $U(r)$ can now be evaluated in any ns state by using Eqs. (17), (20), (22), and (23). Results of this calculation are given in Table III,

TABLE III. Energy eigenvalues as a function of screening parameter for various ns states.

Screening parameter δ	1s		2s		3s		4s	
	Our results	Lam-Varshni (Ref. 14)	Our results	Lam-Varshni (Ref. 14)	Our results	Lam-Varshni (Ref. 14)	Our results	Lam-Varshni (Ref. 14)
0.001	0.499 00	0.499 00	0.124 00	0.124 00	0.054 56	0.054 56	0.030 26	0.030 26
0.002	0.498 00	0.498 00	0.123 01	0.123 01	0.053 58	0.053 58	0.029 30	0.029 30
0.005	0.495 02	0.495 02	0.120 07	0.120 07	0.050 72	0.050 72	0.026 54	0.026 54
0.01	0.490 07	0.490 07	0.115 29	0.115 29	0.046 20	0.046 20	0.022 35	0.022 35
0.02	0.480 30	0.480 30	0.106 15	0.106 15	0.038 01	0.038 01	0.015 32	0.015 33
0.025	0.475 46	0.475 46	0.101 77	0.101 77	0.034 30	0.034 30	0.012 38	0.012 40
0.03	0.470 66	0.470 66	0.097 52	0.097 53	0.030 84	0.030 84	0.009 77	0.009 80
0.04	0.461 17	0.461 17	0.089 39	0.089 40	0.024 56	0.024 56	0.005 42	0.005 50
0.05	0.451 82	0.451 82	0.081 72	0.081 73	0.019 07	0.019 07	0.002 07	0.002 23
0.06	0.442 60	0.442 60	0.074 49	0.074 50	0.014 30	0.014 30	-0.000 40	-0.000 15
0.07	0.433 52	0.433 51	0.067 66	0.067 68	0.010 17	0.010 17		
0.08	0.424 57	0.424 56	0.061 22	0.061 25	0.006 62	0.006 63		
0.09	0.415 74	0.415 74	0.055 15	0.055 19	0.003 61	0.003 61		
0.10	0.407 05	0.407 04	0.049 43	0.049 48	0.001 08	0.001 09		
0.20	0.326 70	0.326 58	0.008 19	0.008 52				
0.25	0.290 67	0.290 43	-0.003 57	-0.003 06				
0.30	0.257 15	0.256 74						
0.40	0.196 98	0.196 10						
0.50	0.145 09	0.143 58						
0.60	0.100 56	0.098 33						
0.70	0.062 67	0.059 68						
0.80	0.030 82	0.027 08						
0.90	0.004 51	0.000 09						
1.00	-0.016 67	-0.021 65						

where we have tabulated energy eigenvalues correct through first order [i. e., E_n of Eq. (7) plus the expectation value of $U(r)$] for a number of values of n and δ . Also given are results obtained by Lam and Varshni by evaluating exactly matrix elements of $U(r)$.

The expansion parameter used in this paper is roughly $1/c_n = \frac{1}{2}n\delta$; thus, for large values of $n\delta$, we see some deviation from the Lam-Varshni results. We could, of course, achieve arbitrarily accurate results by considering more terms in the general expansions given above; however, since we are interested in the properties of the group-theoretical approach rather than in numbers, improved accuracy was not our goal.

Considered as a group-theoretical exercise, we see many similarities between this problem and others which have been previously studied using group theory.^{2,7} The radial wave functions multiplied by a phase function e^{int} form bases for irreducible unitary representations of $SO(2, 1)$. There is also a requirement that one must work in the space of constant n . This requirement appears in a quite different guise here, however, than in the hydrogenic problem. In the hydrogenic case,² the radial variable itself causes the difficulty; here it is the constant c_n . It should be recalled, however, that in the study of the harmonic oscillator,⁷ no

difficulty was encountered in considering matrix elements off-diagonal in n . Thus this difficulty does not appear to be a general result of the group-theoretical approach, but rather a function of the particular central potential.

In order for the group-theoretical approach to be used, it was necessary to expand the perturbing potential in an infinite sum. This sum was then expressed in terms of spherical tensors in $SO(2, 1)$. Each of these tensors is, itself, an infinite sum. Lam and Varshni, on the other hand, evaluated the perturbation $U(r)$ exactly by direct integration. This emphasizes a difficulty of the group-theoretical approach, which is that one must work with spherical tensors rather than directly with the quantities of physical interest. On the other hand, in the present work all matrix elements were evaluated in the very simple ground-state $1s$ configuration, then related to matrix elements in more complicated states via simple coefficients. Lam and Varshni were obliged to work directly with integrals involving very complicated wave functions. Thus, one of the strengths of the group-theoretical approach is that calculations can be carried out in the simplest state (usually the state of lowest n) then related through simple proportionalities to calculations involving more complicated wave functions.

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