

Note

Determination of Accurate Potential Strengths to Yield Specified Eigenvalues of the Radial Schrodinger Equation

The determination of the number of bound states of a system is important in such problems as the existence of a bound state of the helium molecule arising from the interaction of two ground state helium atoms [1] and the highest principal quantum number likely to be observed in radiation from a plasma [2]. In the investigation of this type of problem it is useful to have available a method for obtaining the critical strength or coupling constant of a potential for which it just binds a specified state, i.e., for evaluating $\lambda(l, v)$ for a system of reduced mass μ such that

$$Y_l'' - \left[\frac{2\mu}{\hbar^2} \lambda(l, v) V(r) + \frac{l(l+1)}{r^2} \right] Y_l(r) = 0, \quad (1)$$

has a square integrable solution possessing v nodes. This has been termed the conjugate eigenvalue problem [3].

For fixed λ the problem of determining the eigenvalues E of the potential $V(r)$ has been extensively studied in atomic physics [4], molecular physics [5], and nuclear physics [6], and solutions of high accuracy are easily obtained. It will be shown below that these methods can be modified readily to determine coupling constants λ with comparable facility. Previous methods have involved the determination of the number of zeroes of the inverse of the scattering length [7], simply counting the number of nodes in the wavefunction [8], the use of extrapolation procedures [9], iterative methods [10] and variational methods [11, 12]. The proposed method converges on the critical coupling constant much more readily, essentially because it uses further information from the wavefunction in addition to the number of nodes it contains.

The conjugate eigenvalue problem may be considered as a special case of the problem of determining the coupling constant $\lambda(l, v, E)$ which binds a bound state of energy E . To avoid having to treat the boundary condition of the zero energy problem separately it is convenient to make the Langer transformation $r = \exp(\rho)$, $g_l(\rho) = r^{-1/2} Y_l(r)$ [13], to the Schrodinger equation for arbitrary binding energy, yielding

$$g_l'' + \left\{ - \left(l + \frac{1}{2} \right)^2 - \frac{2\mu}{\hbar^2} [\lambda(l, v, E) U(\rho) - E \exp(2\rho)] \right\} g_l(\rho) = 0, \quad (2)$$

where $U(\rho) = \exp(2\rho) V[\exp(\rho)]$, which is to be solved subject to the condition $g_i(-\infty) = g_i(\infty) = 0$. This transformation may also have some computational advantages [4].

The procedure for obtaining λ is as follows. For specified l and E a trial value of the coupling constant λ_0 is chosen. Two solutions $G_1(\rho)$ and $G_2(\rho)$ are now obtained such that $G_1(-\infty) = G_2(\infty) = 0$. At some point ρ_0 , typically the first maximum occurring in G_2 as it is integrated inwards, $G_1(\rho)$ and $G_2(\rho)$ are scaled to that $G_1(\rho_0) = G_2(\rho_0) = 1$, and their Wronskian, $W(\lambda_0)$, is determined.

The number of nodes in the approximate solution is obtained and if this differs from the specified value then λ_0 must be increased or decreased as appropriate. In practice, little difficulty is experienced in getting the desired number of nodes. At an eigenvalue $W(\lambda) = 0$ and the process of adjusting the trial value corresponds to solving this equation. Newton's method provides a convenient technique, assuming $(dW/d\lambda)_{\lambda_0}$ can be evaluated. This may be obtained by considering the equation satisfied by $h_i(\rho) = dg_i(\rho)/d\lambda$,

$$\frac{d^2 h_i}{d\rho^2} + \left\{ - \left(l + \frac{1}{2} \right)^2 - \frac{2\mu}{\hbar^2} [\lambda U - E \exp(2\rho)] \right\} h_i(\rho) - \frac{2\mu}{\hbar^2} U g_i(\rho) = 0. \quad (3)$$

Multiplying Eq. (3) by $g_i(\rho)$ and Eq. (2) by $h_i(\rho)$ and subtracting

$$(d/d\rho)[g_i(dh_i/d\rho) - h_i(dg_i/d\rho)] = (2\mu/\hbar^2) U(\rho) g_i^2(\rho). \quad (4)$$

Now

$$W(\lambda_0) = G_1(\rho_0) G_2'(\rho_0) - G_2(\rho_0) G_1'(\rho_0) = G_2'(\rho_0) - G_1'(\rho_0),$$

so $dW/d\lambda = H_2'(\rho_0) - H_1'(\rho_0)$, where $H_i(\rho) = dG_i/d\lambda$. Integrating Eq. (4) for G_1 and H_1 from $\rho = -\infty$ to ρ_0 yields

$$H_1'(\rho_0) = \frac{2\mu}{\hbar^2} \int_{-\infty}^{\rho_0} U(\rho) G_1^2(\rho) d\rho,$$

and similarly,

$$H_2'(\rho_0) = - \frac{2\mu}{\hbar^2} \int_{\rho_0}^{\infty} U(\rho) G_2^2(\rho) d\rho,$$

so

$$\left[\frac{dW}{d\lambda} \right]_{\lambda_0} = - \frac{2\mu}{\hbar^2} \int_{-\infty}^{\infty} U(\rho) G^2(\rho) d\rho, \quad (5)$$

where $G = G_1$, $\rho \leq \rho_0$ and $G = G_2$, $\rho \geq \rho_0$. The integral may be evaluated trivially as the solutions are generated. The whole procedure is analogous to that employed by Fox and Mayers [14] for the determination of eigenvalues, except that there a different integral to (5) was evaluated, since (dW/dE) was required.

The finite difference analog of the Wronskian $W(\lambda)$ and the integral (5) using, say, Numerov's method for the numerical integration of Eq. (2) can be obtained similarly to the work of Cooley [15] or Osborne [16]. As with the determination of eigenvalues 4 or 5 iterations are normally sufficient for convergence on a precise value of the coupling constant, whose absolute accuracy is determined by the range of integration and the step sizes employed.

A program to obtain coupling constants has been developed from the eigenvalue program [5] by means of a few simple alterations, the principal one being the evaluation of the integral (5). As a check the coupling constants for the Lennard-Jones (LJ) (10,6) potential were obtained. The LJ(m, n) potential is conveniently written in reduced units as

$$V^*(z) = [1/(m - n)][n/z^m - m/z^n], \quad m > n.$$

In terms of the usual equilibrium separation r_M , well depth ϵ and reduced mass μ , $(2\mu\lambda/\hbar^2) = B = (2\mu\epsilon r_M^2/\hbar^2)$. For the LJ($2n - 2, n$) potentials an analytic solution exists for all values of the angular momentum at zero energy [17], providing a simple check on the program. For $0 \leq v \leq 4$, $0 \leq l \leq 4$, errors of a few parts in 10^7 were achieved for the coupling constants for the LJ(10, 6) potential. As a further check with a potential of a different shape, more typical of atomic or nuclear potentials, the critical binding strengths for the screened Coulomb potential have been evaluated. Excellent agreement was obtained with the values given in [9]. The most commonly used Lennard-Jones potential is the (12, 6) and the coupling constants $B_i(N)$ just required to bind N bound states of angular momentum l are given in Table I for $1 \leq N \leq 5$, and $0 \leq l \leq 4$. The value obtained for $B_0(1)$, 7.04314, agrees with that obtained by Bruch and McGee, quoted in [18]. Other previous values are 7.052 ± 0.001 , [1], 7.07 ± 0.1 [8], 7.047, [11] and 7.044 [12]. The values for $v \geq 1$ and $l = 0$ confirm the less accurate values given in [8].

TABLE I

Values of the coupling constant $B_i(N)$ for the Lennard-Jones (12, 6) potential

$N \backslash l$	0	1	2	3	4
1	7.04314	13.2957	21.4850	31.6095	43.6687
2	46.6170	61.6499	78.5840	97.4307	118.197
3	121.286	145.110	170.821	198.430	227.945
4	231.089	263.700	298.193	334.577	372.857
5	376.028	417.425	460.702	505.864	552.917

In Table II the critical B values are given to bind one s -state for the LJ(m , 6) potential for $8 \leq m \leq 14$. The value for the (9, 6) potential agrees with that obtained in [1, 12].

TABLE II
Values of the coupling constant B to bind one s -state for the Lennard-Jones (m , 6) potential

m	8	9	10	11	12	13	14
B	4.83264	5.43341	6.0 ^a	6.53565	7.04314	7.52489	7.98303

^a Exact value.

It is interesting to compare these exact results with the predictions of the expansion of the semiclassical formula, valid for small l , for a LJ(m , 6) potential [19],

$$B_l(N) = \{[N - \frac{5}{8} - l/4]/\phi(0)\}^2, \quad (6)$$

where $\phi(0)$ has been given explicitly [19] as a function of m . Comparison for the (12, 6) potential shows that Eq. (6) becomes less accurate as l increases with a maximum error of 6.2% for $B_4(1)$, falling to 0.5% for $B_4(5)$. The inclusion of a term in l^2 in Eq. (6) [20] yields even better agreement but for larger l values it is more accurate to employ the complete semiclassical relationship [19, 20]. For the critical B values to bind one s -state for the (m , 6) potential the semiclassical result, Eq. (6) is never in error by more than 5.4%.

This technique for the determination of critical binding strengths, requiring almost trivial alterations of standard eigenvalue routines, enables the conjugate eigenvalue problem to be solved as easily as the normal one and has been shown to yield results of high accuracy for several types of analytic potentials. Its application to potentials whose values are available only at specified points requires the provision of a suitable interpolation scheme which would be required in any case for the determination of other properties of the potential.

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