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Nodal structure of zero-energy wave functions: New approach to Levinson's theorem

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It is well known that minimum principles for energy eigenvalues can be used not only for calculational purposes but also formally as the basis for studies of the nodal structure of the associated eigenfunctions. This formal feature is shown here to have a natural generalization to the zero-energy scattering problem, the scattering length playing the role of the energy eigenvalue in the formulation of the minimum principle. The number of nodes in the zero-energy wave function in a given partial wave for nonrelativistic potential scattering is shown to be equal to the number of negative-energy bound states of the same angular momentum L. Potentials with Coulomb tails are excluded from the present analysis, but will be treated elsewhere. (The connection with classical Sturm-Liouville theory comes perhaps as less of a surprise if one views the zero-energy state as being at the top of the discrete spectrum as well as at the bottom of the continuum.) The result derived here, when combined with the nodal definition of the phase shift along with some information on its threshold behavior, provides us with an alternative derivation of Levinson's theorem relating the zero-energy phase shift for orbital angular momentum L, $\delta_L(0)$, to the number of bound states of the same L. (Very similar results can be derived for potential scattering as described by the Dirac and Klein-Gordon equations.) It may well be possible to extend some of the results obtained here to a number of single-channel multiparticle scattering problems, but this will be discussed elsewhere.

I. INTRODUCTION

The evaluation of a physical quantity may require a knowledge of some trigonometric function of $\delta_L(k)$, the phase shift of the Lth partial wave at an incident energy $E=k^2\hbar^2/2m$, but a knowledge of $\delta_L(k)$ itself is never required; only $\delta_L(k)\text{mod}\pi$ is ever of physical interest. Nevertheless, it can be very useful to have an absolute definition of $\delta_L(k)$. As one example, an application made some time ago, consider a sequence of numerical estimates of phase shifts for the low-energy elastic scattering of electrons and positrons by hydrogen atoms,[1] based on successively larger sets of basis functions in a close-coupling expansion; the errors in the numerical results were difficult to estimate from the calculations themselves. Now it is simple to prove that phase shifts for potential scattering satisfy a monotonicity theorem, namely,

$$\delta_{L2}(k)\geq\delta_{L1}(k) \text{ if } V_1(r)\geq V_2(r) \text{ for all } r ,$$

where δ_{Li} is associated with V_i; the result has meaning if and only if one gives an absolute meaning to δ_L. It is then not surprising, and can be rigorously shown,[2] that the estimate of $\delta_L(k)$ for $e^{\pm}$-atom scattering in a variational calculation is monotonically nondecreasing as one adds basis functions to those already present in the expansion of the trial function, for the addition of functions allow a more adequate description of the virtual excitations of the target; the target can then more easily adapt itself to the incident particle, allowing the effective e^--atom or e^+-atom interaction to become more attractive. However, in some cases $\delta_L(k)\text{mod}\pi$, in radians, seemed to have dropped by a small amount ϵ on the addition of a basis function, although the numerical results which had been obtained for successive calculations suggested that $\delta_L(k)$ had nearly converged.[1] It would have been perfectly possible mathematically to interpret the results as an increase of $\delta_L(k)$ by $\pi-\epsilon$, but it seemed very much more likely that the numerical results were accurate only to order ϵ, and this was confirmed by further numerical studies.[3] We note that sequences of calculations have begun to be made in nuclear reactions—where they are referred to not as close-coupling calculations but as the resonating group method[4]—and absolute definitions of the phase shifts should begin to be useful there too. The fact that the center of mass in the collision of, say, a nucleon and a deuteron is not located at the target, as it effectively is in the scattering of $e^{\pm}$ by an atom, represents an additional degree of complexity in the nuclear case.

One is ultimately interested in scattering by a target with internal degrees of freedom, and elsewhere we will derive some results in connection with the relatively simple but real physical problems of e^+-H, e^--H, and e^+-

He scattering. We will also elsewhere make some remarks on models of $e^{\pm}$-atom and neutron—heavy-nucleus scattering which we believe greatly strengthen previous surmises that $\delta_L(0)$ is a multiple of π, where the multiple is the sum of the number of composite bound states and the number of states of the incident particle excluded by the Pauli principle. However, this paper will be primarily concerned with potential scattering; more specifically, we will obtain information on the nodal structure of the zero-energy scattering wave function by a direct approach. The result can also be obtained by means of a nodal definition of $\delta_L(k)$ combined with a well-known result, Levinson's theorem [see Eqs. (1.2) and (1.3)]. Our result can be viewed as a new kind of derivation of Levinson's theorem; more significantly, it may serve as an opening wedge in the analysis of the zero-energy scattering wave function for a target with internal degrees of freedom. This might serve two quite different purposes. First, it might lead to a useful absolute definition of $\delta_L(0)$ for scattering by such a target, and thereby to a useful absolute definition of $\delta_L(k)$. Second, a knowledge of the nodal structure of the zero-energy wave function can serve as a powerful check on calculations of that wave function or on calculations which involve that wave function. Consider, for example, a calculation of the $L=0$ scattering lengths A_0 which characterize zero-energy scattering of e^+ by a hydrogen atom H or by a helium atom He. If the calculation is based on a variational principle, one has few standards by which to judge the result. One's ability to pass judgment on a calculation is much improved if the calculation is based not just on a variational principle but on a variational bound, for one then knows that the result improves as more basis functions are included, and that of two calculations based on different forms of the trial function the one that generates the lower value of A_0 is the superior one. One has an *additional* criterion if one can show, as one can for e^+-H or e^+-He scattering, that the zero-energy wave function u_0 (u_0 is a function of r_1, r_2, r_{12} for e^+-H, while u_0 is a function of six spatial coordinates for e^+-He) must be nodeless. Thus, having chosen the form of the trial function u_{0t}, and having determined the variational parameters contained in u_{0t} in the course of a calculation based on a variational principle or better a variational bound, a necessary if not sufficient condition for one to expect the variational estimate of A_0 to be reliable would be for u_{0t} to be nodeless.[5]

A. Absolute definition of the phase shift

For short-range potential scattering there are four equivalent definitions of $\delta_L(k)$.

(i) With $V(r)$ and k fixed, we write the scattering wave function as $\sin[\theta_L(r)]$, where $\theta_L(0)=0$, $\theta_L(r)$ is continuous in r, and $\theta_L(r)\sim kr-\frac{1}{2}L\pi+\delta_L(k)$ as $r\sim\infty$.

(ii) A very similar definition is the following. With $V(r)$ and k again fixed, and with $\rho_{Lm}(k)$ and $r_{Lm}(k)$ defined as the mth nodes of the free and true scattering wave functions, with $r=0$ not counted as a node, one has

$$\delta_L(k)=\lim_{m\to\infty} k[\rho_{Lm}(k)-r_{Lm}(k)] . \tag{1.1}$$

(iii) With k fixed but with $V(r)$ replaced by $\lambda V(r)$, the phase shift $\delta_L(k;\lambda)$ associated with $\lambda V(r)$ vanishes for $\lambda=0$ and is continuous in λ, and $\delta_L(k)\equiv\delta_L(k;1)$. This definition cannot readily be extended to, for example, the scattering of an electron by a hydrogen atom; the Pauli principle does not allow one to turn off the interaction between the incident electron and the proton while retaining the e^--p interaction for the e^- initially in the H atom.

(iv) With V fixed, $\delta_L(k)$ vanishes for $k=\infty$ and is continuous in k. This definition is also not readily extended to, say, low-energy e^--H scattering, since, among other things, a phase shift or even eigenphase shifts do not provide a complete description of scattering processes when excitation and ionization are possible; one cannot readily connect high-energy and low-energy phase shifts when the target has internal degrees of freedom.

B. Levinson's theorem

Levinson's theorem states that

$$\delta_L(0)-\delta_L(\infty)=(N_L+\tfrac{1}{2}\xi_L)\pi , \tag{1.2}$$

where N_L is the number of normalizable bound states of angular momentum L—of negative or zero energy—supported by a potential $V(r)$. [More precisely, one must have $r^2V(r)\to 0$ as $r\to 0$, and $r^3V(r)\to 0$ as $r\to\infty$.] The term containing ξ_L represents an interesting subtlety which arises when there exists a bound state of zero energy; one has $\xi_L=0$ for $L>0$, while $\xi_0=0$ if there is no $L=0$ bound state of zero energy and $\xi_0=1$ if there is an $L=0$ bound state of zero energy. (As opposed to the situation for $L>0$, a zero-energy bound state for $L=0$ is not normalizable; such a state has been referred to[6] as a "half-bound state.") For our purposes, it will be convenient to restate the theorem. Since $\delta_L(\infty)=0$ for the potentials allowed by the restrictions $r^2V(r)\to 0$ as $r\to 0$ and $r^3V(r)\to 0$ as $r\to\infty$—Coulombic and hard-core potentials are among those excluded—we have

$$\delta_L(0)=(N_L+\tfrac{1}{2}\xi_L)\pi . \tag{1.3}$$

From our present viewpoint, this version of the theorem has three advantages. First, it concentrates on just the one energy, zero, and it is the nodal structure of the zero-energy scattering wave function $u_L(r)$ which we are here interested in. Second and most importantly, by concentrating on zero energy it enables one, as we will show elsewhere, to extend some aspects of the theorem to be deduced to scattering by a target with internal degrees of freedom; for such a target the use of Levinson's theorem in the form of Eq. (1.2) can be plagued by the theoretical difficulties associated with excitation and breakup in passing from $E=0$ to $E=\infty$, for, as already noted, phase shifts alone no longer represent an adequate description of the various possible processes. Third, it enables one to extend the theorem to cases for which $\delta_L(\infty)\neq 0$, a case in point being relativistic potential scattering. This extension will be presented elsewhere.

The proof of Levinson's theorem as essentially always presented proceeds by using the analyticity properties of the partial wave scattering amplitude $f_L(p)$, where p is the magnitude of the momentum. The elegance and compactness of that proof will not be matched by the present

proof, whose advantage is that it provides complementary information, information about the wave function $u_L(r)$ in coordinate space.

C. The nodal structure of wave functions

The nodal structure of eigenfunctions associated with discrete eigenvalues has for a long time been a subject of great interest to mathematicians. Sturm-Liouville (SL) theory[7] tells us the following:

For a second-order differential equation of rather general form, the number of nodes of an eigenfunction associated with a discrete eigenvalue is exactly equal to the number of eigenstates with eigenvalues below that of the state in question.

The emphasis has been on bounded regions, but the infinite domain has been studied.[7] Our objective will be to obtain the appropriate extension of this theorem to the zero-energy scattering wave functions. Until relatively recently (as measured by the many years which have elapsed since the work of Sturm and Liouville), mathematicians largely ignored scattering theory, many feeling uncomfortable when not in Hilbert space. In fact, the tools for the extension of the theorem to zero-energy scattering exist, for they are based on a variational bound on the scattering length, a result which has been known for some 25 years.[8] Indeed, in many ways the zero-energy state can be looked upon as the highest-energy bound state, a viewpoint to which we will return.

There are two parts to the proof of the theorem for the bound-state case. (Since we are interested in solutions of the Schrödinger equation, we will speak of bound states rather than discrete eigenstates.) First, one proves that the $(n+1)$th eigenfunction $\psi_{n+1}(r)$ has at least one node between any two successive nodes, $r_{n,m}$ and $r_{n,m+1}$, of $\psi_n(r)$. The proof is completely trivial and proceeds canonically. One multiplies the equation satisfied by ψ_n by ψ_{n+1}, that satisfied by ψ_{n+1} by ψ_n, subtracts, integrates from $r_{n,m}$ to $r_{n,m+1}$, and uses Green's theorem to reduce the integral over the terms which arise from the second-derivative terms (the kinetic energy operator in the Schrödinger-equation context) to a surface term. One has $\psi_n(r_{n,m})=\psi_n(r_{n,m+1})=0$ by assumption, and without loss of generality one can choose to have $\psi_n'(r_{n,m})>0$ and $\psi_n'(r_{n,m+1})<0$, where a prime denotes a derivative with respect to r; on the assumption that interlacing does *not* occur, one can without loss of generality choose to have $\psi_{n+1}(r_{n,m})>0$ and $\psi_{n+1}(r_{n,m+1})>0$. One then immediately finds a contradiction, a term of negative sign being equal to a term of positive sign. The extension of this part of the proof to the zero-energy scattering wave function requires no modifications.

The second part of the bound-state proof does require some modifications if one is to obtain an extension to the zero-energy case. The SL bound-state proof is based on the maximum-minimum theorem, to be referred to as the maxi-min theorem. The theorem provides a formal definition of the nth eigenvalue, λ_n. Given that $\psi_n(r)$ satisfies a SL equation, which contains the coefficient functions $p(r)$ and $q(r)$, and assuming that the domain is $0\le r\le\infty$, one considers $n-1$ functions v_i, and seeks the minimum value of the functional

$$D_{\mathrm{SL}}[\psi_{nt}]\equiv\int_0^\infty\left[p(r)\left[\frac{d\psi_{nt}(r)}{dr}\right]^2+q(r)\psi_{nt}^2(r)\right]dr \tag{1.4}$$

over all normalized functions ψ_{nt}, continuous with piecewise continuous derivatives, subject to the restriction that

$$\langle\psi_{nt}\mid v_i\rangle\equiv\int_0^\infty\psi_{nt}(r)v_i(r)dr=0,\quad i=1,\ldots,n-1\ . \tag{1.5}$$

One then chooses new sets of functions v_i, and for each set obtains the minimum of $D_{\mathrm{SL}}[\psi_{nt}]$. λ_n can then be characterized as the maximum of all of the minima; it is attained for $\psi_{nt}=\psi_n$.

Now the entity which characterizes the zero-energy scattering wave function $u_L(r)$ is of course not its energy, which is specified in advance to be zero, but the scattering length A_L, defined, for the short-range potential to which we temporarily restrict ourselves, by

$$u_L(r)\sim-\frac{r^{L+1}}{(2L+1)!!}+\frac{(2L-1)!!A_L}{r^L}$$

$$\equiv-\phi_L(r)+A_L\chi_L(r),\quad r\sim\infty \tag{1.6}$$

where $(-1)!!\equiv1$ and $(2L+1)!!\equiv1\times3\times\cdots(2L+1)$. A functional which formally defines A_L [and which can be used to obtain a variational bound (VB) on A_L] is known.[8] Just as it is particularly simple to obtain a VB on the lowest energy level of given L of a system—a result obtained by Rayleigh but known as the Rayleigh-Ritz (RR) principle—so it is particularly simple to obtain a VB on A_L when there is no bound state of that L, for the zero-energy state is then the lowest-energy state of the system for the given L. One has, in fact,

$$A_L\le D_0[u_{Lt}]=A_{Lt}+(2m/\hbar^2)\langle u_{Lt}\mid H_L\mid u_{Lt}\rangle\ , \tag{1.7}$$

where $H_L=T_L+V$ is the Hamiltonian, with

$$T_L\equiv\frac{\hbar^2}{2m}\left[-\frac{d^2}{dr^2}+\frac{L(L+1)}{r^2}\right], \tag{1.8}$$

and where the trial function $u_{Lt}(r)$ is subject to two boundary conditions: One must choose u_{Lt} such that $u_{Lt}(0)=0$ and such that the asymptotic form of u_{Lt} is that given by Eq. (1.6), with (the unknown) A_L replaced by a trial scattering length A_{Lt}; the subscript zero on D denotes the fact that we are concerned with the no-bound-state case. (We previously denoted by N_L the number of normalizable bound states of angular momentum L. We will also have occasion to use n_L for the number of negative-energy bound states of angular momentum L. A zero-energy bound state for a given L generates an infinite A_L, which we do not wish to consider for the moment, so that in the present case $n_L=N_L$.) If there are N_L bound states, the VB on A_L becomes[8]

$$A_L \le D_{N_L}[u_{Lt}] = A_{Lt} + (2m/\hbar^2)\left[\langle u_{Lt}|H_L|u_{Lt}\rangle - \sum_{m=1}^{N_L} \frac{|\langle u_{Lt}|H_L|\psi_{Lmt}\rangle|^2}{\langle \psi_{Lmt}|H_L|\psi_{Lmt}\rangle}\right]. \tag{1.9a}$$

The N_L trial bound-state functions ψ_{Lmt} must satisfy the conditions

$$\langle \psi_{Lmt}|H_L|\psi_{Lqt}\rangle = E_{Lmt}\delta_{mq}, \quad E_{Lmt} < 0 \tag{1.9b}$$

for all $1 \le m \le N_L$ and $1 \le q \le N_L$, conditions which can always be satisfied in principle and which normally represent no problem in practice; u_{Lt} must satisfy the same boundary conditions as for the no-bound-state case. (It is of crucial importance to the study of scattering by a compound system that, for $N_L \ge 0$, the extension of the VB on A_L to that case from the VB on A_L given above for potential scattering is entirely trivial.) In the original proof that (1.7) or (1.9a) represents a minimum principle, it was assumed that the u_{Lt} are continuous and have continuous first derivatives. For our purposes (see Secs. II B and II C) it will be necessary to enlarge the u_{Lt} allowed to include functions which are continuous but which need only have piecewise continuous first derivatives. We will show in Appendix A that the minimum principle remains valid under these broader conditions.

Just as the VB on A_L provided by Eq. (1.7) is the analog of the RR VB on the ground-state energy, Eq. (1.7) being applicable when the zero-energy scattering state is the state of lowest energy, so the VB on A_L given by Eq. (1.9a) is the analog of the VB on the energy of the N_Lth excited state of the given L. Both are based on what most physicists refer to as the Hylleraas-Undheim principle, in which, as an extension of the RR principle, one finds the ordered eigenvalues of the $N_L \times N_L$ matrix of the Hamiltonian obtained by using N_L trial functions which are supposed to simulate the wave functions of the N_L lowest-lying states; the ordered eigenvalues obtained represent variational bounds on the true ordered eigenvalues. (The difference between VB's on bound-state energy eigenvalues and on A_L is largely a matter of surface term contributions.) The VB on A_L presented above for the no-bound-state case will serve as the functional which provides a formal definition of A_L via a maxi-min theory. This will provide the basis for a proof of the nodal properties of u_L, leading to an alternative derivation of Levinson's theorem. Analysis of the nodal properties can also be based on the VB on A_L presented above in Eq. (1.9a) for the case where N_L bound states exist, without introducing a maxi-min theory explicitly. We present this approach too for the additional insight it provides.

II. THE NODAL STRUCTURE OF ZERO-ENERGY WAVE FUNCTIONS

A. A simple heuristic argument

Before proceeding to formal proofs, it will be useful to present a heuristic argument, one which provides insights not readily gained from a formal approach. We consider here zero-energy potential scattering, where $V(r)$ is short ranged, local, and energy independent, and can support N_L bound states. We first write

$$V = V(r) = V_+(r) + V_-(r),$$

with $V(r) \equiv V_+(r)$ where $V(r) \ge 0$, and $V(r) \equiv V_-(r)$ where $V(r) < 0$. We then introduce

$$V(r;\lambda) \equiv V_+(r) + \lambda V_-(r),$$

where $0 \le \lambda \le 1$. The associated wave function and scattering length will be denoted by $u_L(r;\lambda)$ and $A_L(\lambda)$, respectively. We then, of course, have $V(r;1) = V(r)$, $u_L(r;1) = u_L(r)$, and $A_L(1) = A_L$. Since $V(r;0)$ is never attractive, the curvature of $u_L(r;0)$ is non-negative, $u_L(r;0)$ is nodeless, and $A_L(0)$ is positive. As λ increases, $V(r;\lambda)$ becomes more attractive, and it follows from monotonicity that $A_L(\lambda)$ decreases. If bound states do exist for $\lambda = 1$ then at some value $0 < \lambda_1 < 1$, one will have $|A_L(\lambda_1)| = \infty$, with A_L passing through $-\infty$ to $+\infty$, and $u_L(r;\lambda_1)$, renormalized via division by $A_L(\lambda_1)$, will be proportional to r^{-L}. (We suppress the L dependence of λ_1.) At this point we have a zero-energy normalizable bound state if $L > 0$. If $L = 0$, we have a non-normalizable zero-energy bound state, or—it is somewhat a matter of semantics—a zero-energy scattering state. It will be useful to recall that a solution of the Schrödinger partial wave equation with $V = V(r;\lambda_1)$ and with fixed energy, for $E = 0$ as well as for $E > 0$, which satisfies a specified boundary condition at the origin [$u_L(0;\lambda_1) = 0$], is unique to within a multiplicative factor. Beyond λ_1, the bound-state energy decreases, while the bound-state wave function remains nodeless. $u_L(r;\lambda)$ on the other hand has developed one node. Thus the coefficient of the r^{L+1} term in the asymptotic form of $u_L(r;\lambda_1)$, renormalized by division by A_L, is zero, so that for $L > 0$ $u_L(\infty;\lambda_1) = 0$, with the nodal point of $u_L(r;\lambda)$ moving in from ∞ as λ increases beyond λ_1. For $L = 0$ we have $u_0(r;\lambda_1) \sim$ const as $r \sim \infty$, and $u_0(\infty;\lambda_1) \ne 0$, but $u_0(r;\lambda)$ has a node for $\lambda - \lambda_1 = \epsilon > 0$, however small ϵ is. (Throughout, we will find that for zero-energy bound states one must distinguish between $L = 0$ and $L > 0$.) As λ is increased to 1, there will be, in all, N_L values of λ at which a zero-energy bound state will appear. Each bound-state wave function will have one node more than the number of nodes of the wave function of the bound state just below it, while $u_L(r;\lambda)$ at λ just beyond the value λ_n at which the nth bound state appears will have $n+1$ nodes. The nodal structure of a given bound-state wave function does not change as λ is increased. A node appears in $u_L(r;\lambda)$ at $\lambda = \lambda_n$—infinitesimally beyond for $L = 0$—at $r = \infty$ and moves inward as λ increases. We have throughout assumed that neither $u_L(r;\lambda)$ nor any of the bound-state wave functions can, for some small region of r, dip below zero and thereby introduce two additional nodes, since for that to happen for a function continuous in value and slope would require the function and its derivative to vanish at the same point; the assumption that $V(r)$ is local is crucial to the argument that this cannot happen.

Though the above discussion is far from a proof, it does enable us to more easily "understand" the basic results,

namely, that the number of nodes in the zero-energy wave function for a given partial wave is determined by the total number n_L of negative-energy bound states having the same angular momentum. [Then, using the nodal definition of the phase shift, one may determine $\delta_L(0)$, as discussed below in Sec. II E.] It even has predictive value. Thus, consider a potential which has a repulsive Coulomb component and a second short-ranged component of the type considered above. We have recently shown[9] that a modified version of Levinson's theorem is applicable to this very important case. With $\delta_L(k)$ *redefined* as the phase shift relative to the Coulomb phase, one can prove that

$$\delta_L(0)=N_L\pi\ ,$$

where N_L is the total number of bound states. As opposed to the non-Coulombic case, no distinction need be made here between $L=0$ and $L>0$, even when there is a zero-energy bound state, and this is to be expected on the basis of the argument above, for the nonincreasing Coulomb wave function is a decaying function for all L, including $L=0$.

An unfortunate feature of the heuristic argument is that because of the replacement of $V(r)$ by $V(r;\lambda)$, it will often be impossible to extend the result to scattering by compound systems—the reason is the same as that given for the difficulty in extending the definition of $\delta_L(E)$ based on a study of λV, discussed in Sec. I A, definition (iii). It is then natural to ask if the heuristic argument can be adapted to an analysis based on the VB on A_L, a VB valid for scattering by a compound target as well as for potential scattering. The answer is that, in the same rough spirit, much (but not all) of the adapted argument remains valid. To see this, we begin by noting that the use of Eq. (1.9a) effectively involves the introduction of a non-negative Hamiltonian $\overline{H}_L$—the large parentheses in Eq. (1.9a) can be written in the form $\langle u_{Lt}\,|\,\overline{H}_L\,|\,u_{Lt}\rangle$—constructed by extracting from H_L the effects of the (unknown) bound states through the use of trial functions ψ_{Lmt}. (It is rather nice that one can extract the negative contributions of the bound states, to the extent of making $\overline{H}_L$ non-negative, without knowing the bound-state wave functions.) However, it was later pointed out[10] that one can proceed somewhat differently. One first introduces a simple u_{Lt} which satisfies the boundary conditions at $r=0$ and at $r=\infty$. One then adds functions of specified form, with coefficients to be determined by means of a variational principle; these functions vanish at $r=0$ and at $r=\infty$, so the new u_{Lt} also satisfies the boundary conditions. As one adds functions, one finds the same behavior as that found above on varying λ: the estimate of A_L drops except for N_L jumps, the estimate of $|A_L|$ passing through ∞, with bound states appearing at each jump. There is of course a noninfinitesimal change in the estimate of A_L associated with each addition of a function, while the estimate of A_L varies continuously as λ is varied continuously (except at $\lambda=\lambda_1, \lambda=\lambda_2, \ldots$) but there is a deeper difference. Since the u_{Lt}'s are trial functions and not the solutions of a Schrödinger equation with a local $V(r)$, it is not quite clear that one cannot have $u_{Lt}(r)$, for some region of r, dip below zero. Since we wish to give a proof of the nodal structure of u_L for potential scattering which can, in at least some regards, be extended to scattering by a compound target, we now turn to a more thorough analysis of the VB of Eq. (1.9a). We will also give an analysis based on a functional related to that of Eq. (1.7), for this latter approach is the extension to the $E=0$ wave function u_L of the method described by Courant and Hilbert,[7] and thereby makes more readily useful the abundant literature on the subject.

B. A more formal proof, based on a variational bound on A_L

We now enter into a more formal analysis of the nodal structure of the zero-energy wave function for potential scattering. For the sake of clarity we proceed in steps, beginning with the simplest case in which no bound states of orbital angular momentum L exist, and show that the zero-energy wave function u_L is nodeless. The result is derived by assuming that one or more nodes exist and then showing that this leads to a contradiction. The generalization of the theorem to the case where bound states do exist is taken up subsequently.

The analysis is based on the observation[8] that the scattering length A_L may be characterized as the minimum value, with respect to variations of the trial function u_{Lt}, of the functional $D_0[u_{Lt}]$ given by Eq. (1.7), where u_{Lt} satisfies the condition (1.6). The minimum is attained when u_{Lt} is equal to the exact zero-energy wave function $u_L(r)$ satisfying

$$H_L u_L=0\ . \tag{2.1}$$

Adopting the assumption, which we will show to be false, that $u_L(r)$ has one or more nodes, we let r_0 be the node closest to the origin and define a function $u^{(0)}$ as

$$u^{(0)}(r)=\begin{cases}0, & r\le r_0\\ u_L(r), & r>r_0\ .\end{cases}$$

Accordingly, we have $D_0[u^{(0)}]=A_L$. (This statement is true even though $u^{(0)}$ has a discontinuous first derivative. This point, as well as the more general question of the validity of the minimum principle for such an extended class of trial functions, is addressed in Appendix A.) Now consider the subdomain G_0, with r ranging from r_0 to ∞, contained in the full domain G, for which r ranges from 0 to ∞. We have

$$\min D_0[u_{Lt}]\le A_L$$

in the subdomain G_0, since the value A_L is taken on for the particular choice $u_{Lt}=u^{(0)}$. On the other hand, we have

$$\min D_0[u_{Lt}]\ge A_L$$

in the subdomain G_0, since G_0 is smaller than G (for which the minimum value is A_L) and the decrease in domain decreases the flexibility of the trial function. It follows that the minimum value of $D_0[u_{Lt}]$ in the subdomain G_0 is the true scattering length A_L. To continue, we consider the subdomain G_1, with r ranging from r_1 to ∞, with $0<r_1<r_0<\infty$. Then, with the standard boundary condition at infinity and with $u_{Lt}(r_1)=0$, the result

$$\min D_0[u_{Lt}] = A_L$$

in the subdomain G_1 must hold. This follows from the fact that it holds in G_0 and in G, and that G_1 is contained in G and contains G_0. Let a function which minimizes D_0 in domain G_1, subject to the boundary conditions noted just above, with the minimum value equal to A_L, be represented as $u^{(1)}$. The function $u^{(1)}$ is now extended onto the full domain G by letting $u^{(1)}$ vanish outside G_1. This construction provides us with a function $u^{(1)}$ which satisfies the zero-energy Schrödinger equation except at the point of discontinuity r_1 of the first derivative. However, we have $D_0[u^{(1)}] = A_L$ on the full domain.

We will now show that the assumption that the zero-energy wave function u_L has one or more nodes (with r_0 representing the position of the node nearest to the origin) is false since it leads to a contradiction. Thus, we consider the integral

$$I = \int_{r_1}^{R} \left[\frac{\hbar^2}{2m} \frac{du_L}{dr} \frac{du^{(1)}}{dr} + \left(\frac{\hbar^2}{2m} \frac{L(L+1)}{r^2} + V(r) \right) u_L u^{(1)} \right] dr ,$$

with $u^{(1)}(r_1) = 0$ and $r_1 < r_0$. Integrating by parts in two ways, we obtain

$$I = \int_{r_1}^{R} u_L H_L u^{(1)} dr + \frac{\hbar^2}{2m} \left[u_L \frac{du^{(1)}}{dr} \right] \Bigg|_{r_1}^{R} \tag{2.2a}$$

and

$$I = \int_{r_1}^{R} u^{(1)} H_L u_L dr + \frac{\hbar^2}{2m} \left[u^{(1)} \frac{du_L}{dr} \right] \Bigg|_{r_1}^{R} . \tag{2.2b}$$

Since u_L and $u^{(1)}$ each satisfy the zero-energy Schrödinger equation in the region $r_1 < r < \infty$, the integrals in Eqs. (2.2a) and (2.2b) vanish. Furthermore, we have $u^{(1)}(r_1) = 0$ and the derivative of u_L at r_1 finite. Comparison of Eqs. (2.2a) and (2.2b) then leads to the relation

$$u_L(r_1) \frac{du^{(1)}}{dr} \Bigg|_{r_1} = u_L(R) \frac{du^{(1)}}{dr} \Bigg|_{R} - u^{(1)}(R) \frac{du_L}{dr} \Bigg|_{R} .$$

Taking the limit $R \to \infty$ of the right-hand side, and noting that u_L and $u^{(1)}$ satisfy the same boundary conditions at infinity, with the same scattering length A_L, we obtain

$$u_L(r_1) \frac{du^{(1)}}{dr} \Bigg|_{r_1} = 0 .$$

Since $u^{(1)}$ is a solution of the Schrödinger equation with a local potential, it cannot have a vanishing value and first derivative at the same point. With $(du^{(1)}/dr)|_{r_1} \neq 0$ it follows that $u_L(r_1)$ must vanish and this contradicts our assumption that r_0 is the node of u_L lying closest to the origin. We must conclude that u_L is nodeless if no negative-energy bound states exist.

We consider now the case where one negative-energy bound state exists. (The case where a zero-energy bound state exists is taken up in Sec. II D.) As a first step in the proof that $u_L(r)$ has one node when one bound state exists we prove that it has no more than one node. This is accomplished by appropriate modification of the earlier discussion. We use the fact that the functional whose minimum yields the scattering length is in this case given by $D_1[u_{Lt}]$, defined by Eq. (1.9a) with $N_L = 1$. Let us assume that u_L has two or more nodes and derive a contradiction. Let $\bar{r}_0$ be the position of the node immediately to the right of the first node at r_0. We define the function ϕ_1 to coincide with u_L for $r_0 \leq r \leq \bar{r}_0$ and to vanish elsewhere. Similarly, ϕ_2 coincides with u_L for $r \geq \bar{r}_0$ and vanishes for $r < \bar{r}_0$. We now form the function $\bar{u}^{(0)} = c_1\phi_1 + \phi_2$ with c_1 chosen such that $\bar{u}^{(0)}$ and $H_L\psi_{L1t}$ are orthogonal; $\bar{u}^{(0)}$ is a multiple of u_L in each of the three regions (with coefficients 0, c_1, and 1), and since $u_L(r_0) = u_L(\bar{r}_0) = 0$, $\bar{u}^{(0)}$ is everywhere continuous and has a continuous derivative except at r_0 and $\bar{r}_0$, where it vanishes, and it follows that $D_1[\bar{u}^{(0)}] = A_L$. Using arguments similar to those introduced earlier we may conclude that $\min D_1[u_{Lt}] = A_L$ in the region r_0 to ∞ as well as in the full domain 0 to ∞. The remaining argument leading to a contradiction with the original assumption is then very similar to that given above and we need not repeat it. Having shown that u_L has at most one node we complete the proof by observing that it has at least one node; this is obvious since u_L must be orthogonal to the true bound-state function ψ_{L1} which is known (from standard SL theory) to be nodeless.

The proof that u_L has at most N_L nodes when N_L negative-energy bound states exists follows closely that given above for $N_L = 0$ and $N_L = 1$; the appropriate functional whose minimum gives the scattering length A_L is $D_{N_L}[u_{Lt}]$ defined in Eq. (1.9a). The proof that u_L has precisely N_L nodes is completed by demonstrating that with ψ_{LN_L} representing the bound-state function of the most highly excited state the zero-energy function $u_L(r)$ must have a node between any two consecutive zeros of ψ_{LN_L}. Since ψ_{LN_L} is known to have $N_L - 1$ nodes this leads to the desired result that u_L has N_L nodes. The demonstration is identical to the standard one, sketched in Sec. I C, of the SL theory and need not be repeated here.

C. An alternative proof based on the maxi-min property

The standard analysis of the nodal structure of the SL eigenfunctions is based on the maxi-min property of the eigenvalues.[7] We now indicate how this proof may be generalized to allow for infinite domains and inclusion of inhomogeneous boundary conditions, thereby making it applicable to the zero-energy scattering problem. The functional, the maxi-min property of which we shall formulate, is simply the functional $D_0[u_{Lt}]$ defined by Eq. (1.7), with trial functions u_{Lt} satisfying the condition (1.6). The maxi-min property, for the case where N_L bound states exist and all are of negative energy, is formulated as follows. For each set $\{v_m\}$, $m = 1, \ldots, N_L$, of piecewise continuous functions v_m one obtains the minimum value, to be denoted by $d(v_1, \ldots, v_{N_L})$, of the functional $D_0[u_{Lt}]$. The scattering length A_L is the max-

imum value, with respect to variations of the functions v_m, of these minima. This maximum is obtained for $u_{Lt}=u_L$, the exact solution of $H_L u_L=0$, and for $v_m=\psi_{Lm}$, $m=1,\ldots,N_L$, where the ψ_{Lm} are the exact bound-state solutions. The proof that the scattering length can be characterized by this maxi-min property is presented in Appendix A. With this result established, the proof that the nodes of the zero-energy wave function divide the domain $0\leq r\leq\infty$ into no more than N_L+1 subdomains is very similar to that given in Sec. II B. We show first that if u_L is assumed to have more than N_L nodes the maxi-min procedure applied to the subdomain $r_0\leq r\leq\infty$, denoted as before by G_0, where r_0 is the innermost node of u_L, provides the same value, A_L, as for the full domain. Furthermore, for any subdomain G_i, which contains G_0 and is contained in the full domain G, the maxi-min calculation provides the same result, the exact value of the scattering length; it is obtained for $u_{Lt}=u^{(i)}$, the exact zero-energy solution on this subdomain. An argument identical to that given in Sec. II B allows one to derive a contradiction, showing that the u_L has no more than N_L nodes. It should be noted that this argument has multidimensional generalizations; we will return to this point in a later publication. In the one-dimensional problem to which we are confining our attention one can also show that the zero-energy wave function has at least N_L nodes, the proof being of the standard SL type discussed in Sec. I C. The present discussion serves to emphasize that, as remarked earlier, SL theory has a natural extension to the zero-energy scattering problem.

D. Special cases requiring modification of the formalism

The discussion up to this point has been based on the assumption that the scattering length, as defined by the boundary condition (1.6), exists and is finite. This allowed us to make use of the minimum principle (1.9a) (or, alternatively, the maxi-min principle of Sec. II C) as the starting point of our analysis. We now consider two special circumstances where this procedure requires modification.

1. Bound state at zero energy

As discussed in Sec. II A, the scattering length is infinite if the potential supports a bound state at zero energy. To deal with this case we simply renormalize the wave function, working not with $u_L(r)$ but with $\hat{u}_L(r)\equiv u_L(r)/A_L$. Then, $\hat{u}_L$ behaves asymptotically like r^{-L} for $|A_L|\to\infty$. $\hat{u}_L$ is then normalizable for $L>0$ and its nodal structure can be determined by applying standard SL theory. For $L=0$, $\hat{u}_0$ approaches a constant value asymptotically. While it is not actually normalizable one may introduce a convergence factor $e^{-\alpha r}$, apply bound-state methods to the resultant normalizable function, and then let $\alpha\to 0$. (It was just this limiting procedure which was used originally[8] in the derivation of the minimum principle for A_0.) We conclude that for arbitrary L the number of nodes in the zero-energy wave function $\hat{u}_L$ is equal to the number of bound states in the Lth partial wave with energies lying below zero. (Nodes at $r=0$ or $r=\infty$ are not counted.) A proof based, for example, on the maxi-min property would involve the introduction of the functional

$$\hat{D}[\hat{u}_{Lt}]=\langle\hat{u}_{Lt}\,|\,H_L\,|\,\hat{u}_{Lt}\rangle\,, \tag{2.3}$$

with trial function $\hat{u}_{Lt}\sim(2L-1)!!/r^L$ for $r\sim\infty$, subject to the constraint that it be orthogonal to the set of n_L normalized piecewise continuous functions $v_1,\ldots,v_{n_L}$, where n_L is the number of negative-energy bound states (n_L, it is to be recalled, must be distinguished from N_L, a number which includes not only negative-energy bound states but normalizable zero-energy bound states). The remainder of the proof follows the standard pattern of the SL theory, as discussed in Ref. 7 and reviewed in Sec. II C above.

2. Long-range potentials

Let us now drop the assumption, made in the foregoing discussion, that the potential is of short range and suppose that the potential follows a power-law behavior r^{-s}, $s>3$, asymptotically. No modifications in the previous derivation are required if the inequality $s>2L+3$ is satisfied. However, for $s\leq 2L+3$ the asymptotic form (1.6) is incorrect; there is a term (or terms) in the asymptotic expansion of u_L which dominates over the r^{-L} term. A scattering length, in the usual sense, does not exist in this case.[11] [As an indication of this difficulty we note that the integral $\langle u_{Lt}\,|\,H_L\,|\,u_{Lt}\rangle$ which appears in the functional (1.7) fails to converge for $s<2L+3$ unless the long-range effects of the potential tail are explicitly accounted for in the trial function.]

We now show how the nodal structure of u_L may be determined with the aid of a minimum principle for a modified scattering length defined in terms of asymptotic solutions which account for the effects of the long-range tail of the potential. (This approach is similar in spirit to that used in an earlier discussion of modified effective-range theory.[11]) Thus, we separate the potential into two parts

$$V(r)=V_{\rm sh}(r)+V_l(r)$$

where $V_{\rm sh}$ is of short range, falling off faster than any power of $1/r$, and V_l is a long-range component given by

$$V_l(r)=\begin{cases}0, & r<\bar{r} \qquad (2.4a)\\ -\dfrac{\hbar^2}{2m}\dfrac{\epsilon\beta_s^2}{r^s}, & r>\bar{r} \qquad (2.4b)\end{cases}$$

with $\epsilon=+1$ (attractive) or $\epsilon=-1$ (repulsive). The distance $\bar{r}$ is chosen to be large enough so that V_l cannot support a bound state even for the attractive case. Zero-energy solutions of the Schrödinger equation for the potential V_l, valid for $r>\bar{r}$, can be constructed in terms of Bessel functions, as is well known.[12] Considering first the attractive case ($\epsilon=+1$) we introduce the two linearly independent solutions

$$\chi_{+L}=\Gamma(\nu+1)\left[\frac{s-2}{\beta_s}\right]^{\nu}(2L-1)!!r^{1/2}J_{\nu}(x)\ , \tag{2.5}$$

$$\phi_{+L}=-\frac{\pi}{\Gamma(\nu)}\left[\frac{\beta_s}{s-2}\right]^{\nu}\frac{1}{(2L+1)!!}r^{1/2}N_{\nu}(x)\ , \tag{2.6}$$

where $\nu=(2L+1)/(s-2)$ and

$$x=\left[\frac{2\beta_s}{s-2}\right]r^{-(s-2)/2}\ .$$

The normalization has been chosen to give the same leading terms in the asymptotic expansions as given by χ_L and ϕ_L—and therefore to give unit Wronksian—namely,

$$\chi_{+L}\sim(2L-1)!!/r^{L}\ , \tag{2.7}$$

$$\phi_{+L}\sim r^{L+1}/(2L+1)!!\ , \tag{2.8}$$

for $r\sim\infty$. The correction terms to ϕ_{+L} are significant here. For example, for ν not an integer the next term in the asymptotic expansion of ϕ_{+L} behaves like r^{L-s+3} which dominates over the r^{-L} term for $s<2L+3$. For ν an integer the correction is a logarithmic one. The conclusion that the asymptotic form (1.6) is invalid for $s\leq 2L+3$ follows from these considerations. In the repulsive case ($\epsilon=-1$) we define

$$\chi_{-L}(r)=\Gamma(\nu+1)\left[\frac{s-2}{\beta_s}\right]^{\nu}(2L-1)!!r^{1/2}I_{\nu}(x)\ , \tag{2.9}$$

$$\phi_{-L}(r)=\frac{2}{\Gamma(\nu)}\left[\frac{\beta_s}{s-2}\right]^{\nu}\frac{1}{(2L+1)!!}r^{1/2}K_{\nu}(x)\ . \tag{2.10}$$

The leading terms in the asymptotic expansions of χ_{-L} and ϕ_{-L} are as shown in Eqs. (2.7) and (2.8), respectively; again, correction terms are significant for $s\leq 2L+3$.

We now introduce zero-energy solutions of the Schrödinger equation for the full potential $V(r)$ denoted as u_{+L} (for $\epsilon=1$) and u_{-L} (for $\epsilon=-1$) which satisfy the boundary conditions

$$u_{\pm L}(0)=0\ , \tag{2.11a}$$

$$u_{\pm L}(r)\sim-\phi_{\pm L}(r)+B_{\pm L}\chi_{\pm L}(r),\quad r\sim\infty\ . \tag{2.11b}$$

The parameters $B_{\pm L}$ play the role of modified scattering lengths. In analogy with the minimum principle of Eq. (1.9a), if N_L bound states exist and all are of negative energy, the $B_{\pm L}$ satisfy

$$B_{\pm L}\leq D_{\pm N_L}[u_{\pm Lt}]$$
$$=B_{\pm Lt}+\frac{2m}{\hbar^2}\left[\langle u_{\pm Lt}\,|\,H_L\,|\,u_{\pm Lt}\rangle-\sum_{m=1}^{N_L}\frac{|\langle u_{\pm Lt}\,|\,H_L\,|\,\psi_{Lmt}\rangle|^2}{\langle\psi_{Lmt}\,|\,H_L\,|\,\psi_{Lmt}\rangle}\right], \tag{2.12}$$

where the N_L trial bound-state functions satisfy Eqs. (1.9b) and where $u_{\pm Lt}$ satisfies boundary conditions of the form shown in Eqs. (2.11) with $B_{\pm L}$ replaced by $B_{\pm Lt}$. The same arguments developed earlier for short-range potentials now lead to the conclusion that the number of nodes in the zero-energy wave function is equal to the number of bound states of negative energy. This statement requires no modification in the case where a bound state exists at zero energy, although the derivation must be modified slightly as discussed in Sec. II D 1.

E. Zero-energy phase shift and Levinson's theorem

From the fact that the zero-energy wave function has n_L nodes (where n_L, it will be recalled, is the number of negative-energy bound states) we will show that the zero-energy phase shift $\delta_L(0)$ satisfies Levinson's theorem, Eq. (1.3). Thus, let R be a fixed point well outside the range of the potential (in this discussion, for simplicity, we assume short-range potentials), and such that each of the nodes of the zero-energy wave function lies to the left of R. Consider now the solution $w_L(r,k)$ of the Schrödinger equation

$$H_L w_L(r,k)=(\hbar^2/2m)k^2 w_L(r,k) \tag{2.13}$$

for a scattering energy so low that there exists a subinterval S such that $R<r\ll(L+\frac{1}{2})/k$. In the range $r>R$, $w_L(r,k)$ approaches a linear combination of free solutions,

$$w_L(r,k)\sim k^L\{\cot[\delta_L(k)]krj_L(kr)-krn_L(kr)\}\ , \tag{2.14}$$

and in the subinterval $R<r\ll(L+\frac{1}{2})/k$ the energy term $E=\hbar^2k^2/2m$ as well as the potential can be neglected in the Schrödinger equation. Therefore, for $r\ll(L+\frac{1}{2})/k$, $w_L(r,k)$ is proportional to the zero-energy solution and in the subinterval S the solution $w_L(r,k)$ is approximately equal to the asymptotic form of the zero-energy solution. Furthermore, there are no nodes of $w_L(r,k)$ in this subinterval. The free solution $krj_L(kr)$ is nodeless in the whole range $r\ll(L+\frac{1}{2})/k$. The energy-dependent nodes of both solutions lie to the right of this subinterval and interlace each other. [Interlacing is a general property of two linearly independent solutions of a given Schrödinger equation, that is, with the same potential and the same energy E; in the present context, we are in the region where $V(r)$ is negligible, so that $w_L(k,r)$ and $krj_L(kr)$ both satisfy the Schrödinger equation for a free particle.] $\delta_L(k)$ of course represents the asymptotic phase difference between $w_L(r,k)$ and $krj_L(kr)$. It will be convenient to introduce $\tilde{\delta}_L(k)$, defined by

$$\delta_L(k)=n_L\pi+\tilde{\delta}_L(k)\ . \tag{2.15}$$

From the nodal definition of $\delta_L(k)$, we can conclude that for $k\ll(L+\frac{1}{2})/R$

$$-\pi\leq\tilde{\delta}_L(k)\leq\pi\ . \tag{2.16}$$

The sign of $\tilde{\delta}_L(k)$ depends on the relative position of the first energy-dependent nodes of $w_L(r,k)$ and $krj_L(kr)$. If it is the node of $w_L(r,k)$ (in the range $r>R$) which is

nearer to the origin then $\tilde{\delta}_L(k) \geq 0$, otherwise $\tilde{\delta}_L(k) \leq 0$. The knowledge of this relative position, along with the known threshold behavior of $\cot\delta_L(k)$, leads to the conclusion that $\tilde{\delta}_L(k)$ vanishes for $k \to 0$ (details of the proof are given in Appendix B) and therefore that $\delta_L(0)$ is $N_L\pi$. (Note that $n_L = N_L$ since we have assumed here that there are no zero-energy bound states.)

Special attention must be given to the situation where a zero-energy bound state exists. (This is indicated by the fact that $k^{2L+1}\cot\delta_L$ vanishes at $k=0$ for A_L infinite and the next term in the energy expansion has to be investigated.) One can determine $\delta_L(0)$ in this case directly by a limiting procedure, using the nodal definition of the phase shift, in analogy with the preceding discussion. This leads to Levinson's theorem, Eq. (1.3); see Appendix B for details of the proof.

To summarize, we have combined the theorem dealing with the number of nodes of the zero-energy wave function with both the nodal definition of the phase shift $\delta_L(k)$ and our knowledge of the low-energy behavior (modulo π) of the phase shift to arrive at Levinson's theorem in the form stated in Eq. (1.3).

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APPENDIX A: MINIMUM PRINCIPLE FOR THE SCATTERING LENGTH, AND THE MAXI-MIN PRINCIPLE

We will prove first that the variational upper bound on A_L developed in Ref. 8 remains valid if one extends the class of trial functions from functions u_{Lt}, which are continuous and have continuous first derivatives, to functions u_{Lt} such that u_{Lt} is continuous and u'_{Lt} is piecewise continuous. The original class is quite sufficient for obtaining numerical values for the upper bound. The formal proof concerning the number of nodes of u_L, however, requires the wider class of trial functions. (In our proof, discontinuities of first derivatives arise only at points where u_{Lt} vanishes. In fact, the minimum principle holds under less restrictive conditions; we will show that it is valid for all continuous functions with piecewise continuous derivatives.) The meaning of the derivatives of discontinuous functions is given in terms of the step function and its derivative—the δ function. Note that the class of functions one allows in the minimum principle is identical with the class used by Courant and Hilbert[7] in their study of the SL functional given in Eq. (1.4); note too that the SL functional involves first derivatives of the trial function, while the functional which represents an upper variational bound on A_L involves second derivatives. One can work with either form in a bound-state problem, but in a scattering problem one must work with the second derivatives of the trial function in order to eliminate a surface term at infinity.

The minimum principle for A_L of Ref. 8 is provided by the functional $D_{N_L}[u_{Lt}]$ given by Eq. (1.9a), with u_{Lt} and u'_{Lt} continuous. To prove that the principle remains valid for u_{Lt} continuous and u'_{Lt} piecewise continuous we begin by transforming $D_{N_L}[u_{Lt}]$ into a functional of the error function $\delta u_L \equiv u_{Lt} - u_L$. The reasons for the transformation are, first, that δu_L is better behaved at infinity than is u_L, and second, that we can make use of properties of $D_{\rm SL}$ proved by Courant and Hilbert. More precisely, we will show that

$$D_{N_L}[u_{Lt}] = A_L + D_{\rm SL}[\delta u_L] - \frac{2m}{\hbar^2}\sum_{m=1}^{N_L}\frac{|\langle \delta u_L | H_L | \psi_{Lmt}\rangle|^2}{E_{Lmt}}, \tag{A1}$$

where $D_{\rm SL}[\delta u_L]$ is defined by Eq. (1.4), with $p(r)=1$ and

$$q(r) = [L(L+1)/r^2] + (2m/\hbar^2)V(r),$$

and where the conditions satisfied by the $\psi_{Lmt}(r)$ are defined by Eq. (1.9b); in particular, we have

$$E_{Lmt} = \langle \psi_{Lmt} | H_L | \psi_{Lmt}\rangle < 0 .$$

From the boundary conditions satisfied by u_L and u_{Lt}, it follows that

$$\delta u_L \sim (A_{Lt} - A_L)(2L-1)!!r^{-L}, \quad r \sim \infty .$$

δu_L is normalizable for $L > 0$, while δu_0 is not normalizable but can be made so by the introduction of a convergence factor, as discussed above in connection with a closely related point, and as justified in Ref. 8.

We are now in a position to prove Eq. (A1). We begin by introducing

$$I \equiv (2m/\hbar^2)(\langle u_L | H_L | u_{Lt}\rangle - \langle u_{Lt} | H_L | u_L\rangle) .$$

Since $H_L u_L = 0$, we have, on the one hand,

$$I = (2m/\hbar^2)\langle u_L | H_L | u_{Lt}\rangle .$$

On the other hand, we can cancel the potential and angular momentum terms in the second set of parentheses, and we can then use Green's theorem to write I as a sum of surface terms, at the origin and at ∞,

$$I = S_0 + S_\infty .$$

(One can easily check that there are no contributions from the discontinuities of first derivatives.) S_0 vanishes, $S_\infty = A_L - A_{Lt}$, and we therefore have

$$(\hbar^2/2m)(A_L - A_{Lt}) = \langle u_L | H_L | u_{Lt}\rangle = \langle u_{Lt} | H_L | u_{Lt}\rangle - \langle \delta u_L | H_L | \delta u_L\rangle . \tag{A2}$$

This proves that the usual identity is valid for the wider class of functions. Integrating by parts once, and using the fact that δu_L vanishes at the origin and either vanishes ($L > 0$) or approaches a constant ($L = 0$) at infinity, we may rewrite the last term in Eq. (A2) as

$$(2m/\hbar^2)\langle \delta u_L | H_L | \delta u_L\rangle = D_{\rm SL}[\delta u_L] . \tag{A3}$$

[We note that (A3) is then valid for δu_L continuous and

$\delta u_L'$ piecewise continuous, as well as for δu_L and $\delta u_L'$ continuous.] We also have

$$\langle u_L \mid H_L \mid \psi_{Lmt} \rangle = \langle H_L u_L \mid \psi_{Lmt} \rangle = 0 \ .$$

Furthermore, since H_L is Hermitian even for the wider class of functions, we have

$$\langle \delta u_L \mid H_L \mid \psi_{Lmt} \rangle = \langle \psi_{Lmt} \mid H_L \mid \delta u_L \rangle \ ,$$

and

$$\langle u_{Lt} \mid H_L \mid \psi_{Lmt} \rangle = \langle \delta u_L \mid H_L \mid \psi_{Lmt} \rangle \ . \tag{A4}$$

The use of Eqs. (A2)—(A4) in the definition of Eq. (1.9a) of D_{N_L} gives (A1).

Letting $\mathscr{S}$ represent the sum term in Eq. (A1), we have

$$D_{N_L}[u_{Lt}] - A_L = D_{\mathrm{SL}}[\delta u_L] + \mathscr{S} \ , \tag{A5}$$

and the proof which we seek, that (i) $D_{N_L}[u_{Lt}] - A_L \geq 0$, reduces to the proof that (ii) $D_{\mathrm{SL}}[\delta u_L] + \mathscr{S} \geq 0$. We wish to prove that (i) is valid for the wider class of trial functions, but all we know thus far, from the result of Ref. 8, is that (i) is valid for u_{Lt} and u_{Lt}' continuous. It is of course then true that (ii) is valid for δu_{Lt} and $\delta u_{Lt}'$ continuous. For the bound-state case, for which $D_{\mathrm{SL}}[u_{Lt}]$ is bounded from below for u_{Lt} and u_{Lt}' continuous, Courant and Hilbert show that the lower bound remains valid for u_{Lt} continuous and u_{Lt}' piecewise continuous. (They invoke the Weierstrass theorem which enables one to approximate—in the mean—the piecewise continuous function u_{Lt}' by a continuous function ϕ' and, at the same time, to approximate u_{Lt} by ϕ, an integral of ϕ'.) By a very similar argument, one can show that the lower bound of zero on $D_{\mathrm{SL}}[\delta u_L] + \mathscr{S}$, and therefore the lower bound of zero on $D_{N_L}[u_{Lt}] - A_L$, is preserved when one allows u_{Lt}' to be piecewise continuous rather than continuous.

We obtain some insight into the above result by arguing physically rather than formally. In an expression such as $\langle \delta u \mid V \mid \delta u \rangle$, it can make little difference, for δu continuous, with piecewise continuous first derivatives, if we replace δu by a smoothed out version. With T_L the kinetic energy operator, it is by no means obvious that the same is true for $\langle \delta u \mid T_L \mid \delta u \rangle \equiv \langle T_L \rangle$, but if there is a change in the value of $\langle T_L \rangle$ we expect $\langle T_L \rangle$ to be greater for a continuous function δu_1 for which $\delta u_1'$ is piecewise continuous than for a continuous function δu_2 which approximates δu_1 and for which $\delta u_2'$ is continuous, since $\langle T_L \rangle$ tends to be smaller for smoother functions.

We turn now to the proof that the functional $D_0[u_{Lt}]$ of Eq. (1.7) represents a maxi-min principle for the determination of A_L when N_L negative-energy bound states exist.

To begin our study of the functional $D_0[u_{Lt}]$ we note that by Eq. (A1) we have

$$D_0[u_{Lt}] = A_L + D_{\mathrm{SL}}[\delta u_L] \ . \tag{A6}$$

Let us first verify that the minimum value of $D_0[u_{Lt}]$ is A_L if the u_{Lt} are chosen to be orthogonal to each of the ψ_{Lm}. Since $\langle u_L \mid \psi_{Lm} \rangle = 0$ for all m, the assumption that $\langle u_{Lt} \mid \psi_{Lm} \rangle = 0$ for all m gives $\langle \delta u_L \mid \psi_{Lm} \rangle = 0$ for all m. But the latter set of conditions are precisely those for which $D_{\mathrm{SL}}[\delta u_L] \geq 0$ since the $\mathscr{S}$ term in (A5) is then equal to 0. That gives the desired result that $D_0[u_{Lt}] \geq A_L$ if $\langle u_{Lt} \mid \psi_{Lm} \rangle = 0$ for all m.

Now suppose, as required in the maxi-min construction, that u_{Lt} is orthogonal not to the set $\{\psi_{Lm}\}$ but to the set $\{v_m\}$, $m = 1,2,\ldots,N_L$, consisting of functions which are normalizable and linearly independent but otherwise arbitrary. We observe that for any set $\{v_m\}$ the minimum value of $D[u_{Lt}]$ cannot exceed A_L. In fact, for the particular (formal) choice of trial function

$$\tilde{u}_{Lt} = u_L + \sum_{m=1}^{N_L} c_m \psi_{Lm} \ ,$$

with coefficients c_m selected to satisfy the orthogonality conditions $\langle \tilde{u}_{Lt} \mid v_m \rangle = 0$, $m = 1,2,\ldots,N_L$, one finds

$$D_0[\tilde{u}_{Lt}] = A_L + \sum_{m=1}^{N_L} c_m^2 E_{Lm} \leq A_L \ .$$

We may therefore conclude that the maximum (with respect to variations in the functions v_m) of the minimum value of $D_0[u_{Lt}]$ is the true scattering length A_L; this is the maxi-min property used in Sec. II C of the text.

APPENDIX B: THE CONNECTION BETWEEN THE NUMBER OF NODES OF THE ZERO-ENERGY WAVE FUNCTION AND THE ZERO-ENERGY PHASE SHIFT

In this appendix we assume throughout, for simplicity, that the potential is of short range. We assume further, temporarily, that A_L is finite. (The case for which A_L is infinite will be discussed shortly.) We begin by listing some properties of the wave function in different domains.

It will be useful to introduce a point R which satisfies two conditions:

(i) it lies well beyond the range r_p of the potential and

(ii) it lies well beyond the last node, if there are any nodes, of the zero-energy wave function $u_L(r)$.

We seek to connect the zero-energy scattering parameter, the scattering length A_L, with the positive energy scattering parameter, the phase shift $\delta_L(k)$. To do so, it is sufficient to consider arbitrarily small values of k. [Since $\delta_L(k)$ is by definition continuous in k, its absolute determination at any k, and in particular at very small k, generates an absolute definition at all k.] With R fixed, we consider values of k so small that the condition

$$kR \ll L + \tfrac{1}{2}$$

is satisfied. Beyond r_p the Schrödinger wave function $w_L(r,k)$ reduces to a linear combination of free solutions and is given by Eq. (2.14). In the interval $r_p < r \ll (L+\frac{1}{2})/k$, one can neglect the energy term in the Schrödinger equation; this is equivalent to replacing j_L and $n_L(kr)$ in (2.14) by their small argument forms, and $k^{2L+1}\cot\delta_L(k)$ by its threshold value, $-1/A_L$. We have

$$w_L(r,k) \approx u_L(r) \approx -\frac{1}{A_L}\frac{r^{L+1}}{(2L+1)!!} + \frac{(2L-1)!!}{r^L} \ , \qquad r_p < r \ll \frac{L+\frac{1}{2}}{k} \ . \tag{B1}$$

In the interval $R<r\ll(L+\frac{1}{2})/k$, the first term dominates—the zero-energy wave function would otherwise have a node for $r>R$—and we have

$$w_L(r,k)\approx-\frac{1}{A_L}\frac{r^{L+1}}{(2L+1)!!},\quad R\ll r\ll\frac{(L+\frac{1}{2})}{k}\ . \tag{B2}$$

Choosing the free regular solution $\phi_L(r,k)$ to be normalized as

$$\phi_L(r,k)=krj_L(kr)/k^{L+1}\ ,$$

we have

$$\phi_L(r,k)\approx r^{L+1}/(2L+1)!!,\quad r\ll(L+\tfrac{1}{2})/k\ .$$

$\phi_L(r,k)$ is clearly positive and nodeless for $r\ll(L+\frac{1}{2})/k$. The nodes of $w_L(r,k)$ in the range $r\ll(L+\frac{1}{2})/k$ are very close to the nodes of $w_L(r,0)$ for the small k under consideration and lie to the left of R; $w_L(r,k)$ has no nodes in the interval R to $(L+\frac{1}{2})/k$. Both $w_L(r,k)$ and $\phi_L(r,k)$ are oscillatory beyond $(L+\frac{1}{2})/k$, and their (energy-dependent) nodes interlace in that region; the proof that they interlace is similar to the proof given in Sec. I C that the nodes of $\psi_{n+1}(r)$ and $\psi_n(r)$ interlace.

We can obtain further information about $w_L(r,k)$ by studying the Wronksian

$$W[w_L,\phi_L]\equiv w_L(r,k)\phi_L'(r,k)-w_L'(r,k)\phi_L(r,k)\ ,$$

where a prime denotes differentiation with respect to r. We then have

$$W'[w_L,\phi_L]=w_L\phi_L''-w_L''\phi_L=-(2m/\hbar^2)V(r)w_L\phi_L\ ,$$

where the second step following on using the differential equations satisfied by w_L and ϕ_L. It follows that $W'\approx0$ for $r>r_p$, and therefore that $W[w_L,\phi_L]\approx$const for $r>r_p$. The constant is found to be unity by studying very large r, where w_L and ϕ_L are known. We therefore have

$$w_L(r,k)\phi_L'(r,k)-w_L'(r,k)\phi_L(r,k)\approx1,\quad r>r_p\ . \tag{B3}$$

The value of $\delta_L(k)\mathrm{mod}\pi$, all that is used in calculations of physical quantities, follows, of course, from a comparison of the phases of $w_L(r,k)$ and $\phi_L(r,k)$ at asymptotically large r. However, we are seeking to define and determine the absolute value of $\delta_L(k)$. For sufficiently small k and for A_L finite, our present concern, we can deduce additional information about $\delta_L(k)$ from its nodal definition. Thus, $w_L(r,k)$ has n_L nodes in the interval 0 to R and no nodes in the interval R to $(L+\frac{1}{2})/k$, while ϕ_L has no nodes in the entire interval 0 to $(L+\frac{1}{2})/k$; moreover, the energy-dependent nodes of w_L and of ϕ_L not only interlace, but each set of nodes has a spacing of π asymptotically. It follows that $\delta_L(k)$ must be something like $n_L\pi$; more precisely, we deduce that $|\delta_L(k)-n_L\pi|\leq\pi$. The two pieces of information, the knowledge of $\delta_L(k)$ modulo π and the inequality just obtained, allow only two possibilities for the correct value of $\delta_L(k)$. [If $\delta_L(k)\mathrm{mod}\pi$ is identically zero, there are three possibilities *a priori*.] In terms of $\tilde{\delta}_L(k)\equiv\delta_L(k)-n_L\pi$, we have $-\pi\leq\tilde{\delta}_L(k)\leq\pi$, and the correct choice between the two possibilities for $\delta_L(k)$ reduces to the determination of the sign of $\tilde{\delta}_L(k)$. The sign is determined by the relative positions of the first energy-dependent nodes of $w_L(r,k)$ and $\phi_L(r,k)$. To find the relative position, we let R_{1L} denote the first node of $\phi_L(r,k)$; R_{1L} will be well beyond $(L+\frac{1}{2})/k$. We then have $\phi_L(R_1,k)=0$ and $\phi_L'(R_{1L},k)<0$. We conclude from Eq. (B3) that $w_L(R_{1L},k)<0$. Since the sign of $w_L(r,k)$ in the region $R\ll r\ll(L+\frac{1}{2})/k$ is determined by the sign of A_L [see Eq. (B2)], we must distinguish between $A_L<0$ and $A_L>0$. If $A_L<0$, $w_L(r,k)$ is positive in its nodeless region, $R<r\ll(L+\frac{1}{2})/k$, but has become negative at the location R_{1L} of the first node of $\phi_L(r,k)$, that is, the first energy-dependent node of w_L lies to the left of the first node of ϕ_L, so that $0\leq\tilde{\delta}_L(k)\leq\pi$. If $A_L>0$, then $w_L(r,k)$ is negative in its nodeless region and remains negative out to the value R_{1L} of the first node of ϕ_L, that is, the first node of w_L lies to the right of the first node of ϕ_L, so that $-\pi\leq\tilde{\delta}_L(k)\leq0$. In either case $\delta_L(k)$ is uniquely determined. [It might be helpful to remark that with the boundary conditions given the sign of $u_L(r)$ and of $w_L(r,k)$ for r close to the origin need not be positive, so that the sign of u_L and of w_L in the nodeless region is not determined by the number n_L of nodes of u_L.]

Since $\cot[\tilde{\delta}_L(k)]=\cot[\delta_L(k)]$, we can write the usual threshold law as

$$\lim_{k\to0}k^{2L+1}\cot[\tilde{\delta}_L(k)]=-\frac{1}{A_L}\ .$$

It follows that $\cot\tilde{\delta}_L(0)$ is $-\infty$ for $A_L>0$ and $+\infty$ for $A_L<0$. Combined with the ranges for $\delta_L(k)$ deduced just above for $A_L<0$ and for $A_L>0$, we find that in either case we have $\tilde{\delta}_L(0)=0$, and therefore $\delta_L(0)=n_L\pi$. [Since $\tilde{\delta}_L(0)=0$ for $A_L<0$ and for $A_L>0$, it follows by continuity that $\tilde{\delta}_L(0)=0$ for $A_L=0$.]

We turn now from A_L finite to the rather special case for which $|A_L|=\infty$; there is then a bound state at zero energy, and $w_L(r,k)$ in the subinterval $R<r\ll(L+\frac{1}{2})/k$ is given by the second term of the right-hand side of Eq. (B1) and is therefore positive. The result obtained for A_L finite, that $w_L(R_{L1},k)<0$, remains valid for $|A_L|=\infty$, so that w_L changed sign between $(L+\frac{1}{2})/k$ and R_{L1}, that is, the first energy-dependent node of w_L lies to the left of R_{1L}, and we conclude that $0<\tilde{\delta}_L(k)<\pi$. To proceed further we note that for $1/A_L=0$ effective range theory gives

$$k^{2L+1}\cot[\delta_L(k)]\approx\tfrac{1}{2}r_Lk^2$$

for the small k under consideration, where r_L is the effective range. Since $\cot\tilde{\delta}_L(k)=\cot[\delta_L(k)]$, we see that $\cot[\tilde{\delta}_0(0)]=0$, and therefore that $\tilde{\delta}_0(0)=\frac{1}{2}\pi$. From now on we can restrict our considerations to $L\geq1$. We will show that $r_L<0$ for $1/A_L=0$. For $L=1$ or 2 this result follows directly from explicit expressions for r_L;[13] for the extension to arbitrary L, it will prove to be more convenient to derive alternative expressions for r_L. To this end we consider the limit as $|A_L|\to\infty$ of $\hat{u}_L(r)$, defined as in Sec. II D by $\hat{u}_L(r)=u_L(r)/A_L$. [Since $u_L(r)$ contains A_L, $\hat{u}_L$ does not vanish as $|A_L|\to\infty$.] We

then multiply the Schrödinger equation for w_L by $\hat{u}_L$ and the Schrödinger equation for $\hat{u}_L$ by w_L, subtract, and integrate from 0 to a, where

$$R < a \ll (L+\tfrac{1}{2})/k \ .$$

Introducing the logarithmic derivative of w_L,

$$\mathscr{L} \equiv w_L'(a,k)/w_L(a,k) \ , \tag{B4}$$

we find that

$$\mathscr{L} = [\hat{u}\,'_L(a)/\hat{u}_L(a)] - k^2 b(k) \ ,$$

where

$$b(k) \equiv \int_0^a \hat{u}_L(r) w_L(r,k) dr / \hat{u}_L(a) w_L(a,k) \ .$$

Corrections to $b(0)$ which are of order k^2 give corrections to $\mathscr{L}$ which are of order k^4, and can be ignored. We therefore have

$$b(k) \approx b(0) = \left[\int_0^a dr\, \hat{u}_L^{\,2}(r)/\hat{u}_L^{\,2}(a) \right] > 0 \ .$$

For R sufficiently large, $\hat{u}_L(r) \approx (2L-1)!!\, r^{-L}$ in the region which includes the point a (there is no r^{L+1} term for $|A_L| = \infty$) and therefore $\hat{u}\,'_L(a)/\hat{u}_L(a) \approx -L/a$. We can now write

$$\mathscr{L} = -(L/a) - k^2 b(0) + O(k^4) \ .$$

We can also calculate $\mathscr{L}$ by using Eq. (B4) and the form of $w_L(r,k)$ appropriate to the region which includes the point a, namely, the form given by Eq. (2.14). This form can be simplified, since for the region in question one can use the small argument expansions of $j_L(kr)$ and $n_L(kr)$. Equating the two expressions for $\mathscr{L}$, one arrives at

$$\tfrac{1}{2} r_L = -\int_0^a \hat{u}_L^2(r) dr - [(2L-1)!!]^2/[(2L-1)a^{2L-1}] \ .$$

Since we are concerned only with $L \geq 1$, we see immediately from this formula that $r_L < 0$. (It is easy to check that $dr_L/da = 0$, so that, as must be the case if the result is to be meaningful, r_L is negative for any a in the prescribed domain.) It follows that $\cot[\delta_L(0)] = \cot[\tilde{\delta}_L(0)] = -\infty$. Since $\tilde{\delta}_L(0)$ is to be understood as the limit as $k \to 0$ from above, we conclude that $\tilde{\delta}_L(0) = \pi$.

The proof as presented is valid for any short-range potential, that is, for any $V(r)$ which falls off faster than any power of $1/r$. The proof for long-range potentials is more complicated but proceeds along similar lines and will not be presented here.

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