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Additional WKB Inversion Relations
for Bound-State and Scattering Problems*

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ABSTRACT

New inversion relations for the diatom system (elastic scattering of two atoms by a single potential, or a bound diatomic molecule) are presented. They are exact within the WKB approximation for the relevant quantities and are closely related to the well-known RKR expressions. Explicit formulae are given for bound-state and scattering input.

I. Introduction

There has been a great deal of interest recently in the development of inversion methods¹⁻³--that is, methods for determining intermolecular potentials directly from experimental data, rather than assuming some parameterized form for the potential and adjusting the parameters to fit the data. With regard to the elastic scattering of two atoms, for example, one desires an explicit procedure whereby the experimentally obtained cross section can be used to generate the interatomic potential $V(r)$ which gives rise to the observed scattering.

In this paper some new inversion formulae for atom-atom systems are presented, all of which are based on the WKB approximation for the quantities involved; they are closely related to the Rydberg-Kein-Rees (RKR) method⁴ for determining a potential well from its eigenvalues. Section II summarizes the RKR method and presents the new formulae as they pertain to bound-state problems; Section III considers the form taken by the inversion relations for the case of elastic scattering.

In applying any of these formulae to invert scattering data, the principle difficulty remains the problem of extracting the scattering phase shifts from the observed cross sections; it is the phase shifts which are required for the inversion formulae. It is, in general, possible to accomplish this,² but very accurate data may be required.¹ In some special cases it can be accomplished very easily; see, for example, the application at the end of Section III.

II. Inversion from Eigenvalues

First we summarize the RKR method.⁴ The vibrational-rotational eigenvalues $E(n, \ell)$ for the diatomic molecule are assumed known from

experiment; the problem is to determine the potential $V(r)$.

The WKB eigenvalue relation is⁵

$$(n + \frac{1}{2})\pi = \int_{r_{<}}^{r_{>}} dr \{2\mu[E - V(r)] n^2 - \ell^2/r^2\}^{\frac{1}{2}} \quad (1)$$

where $r_{\leq} = r_{\leq}(E, \ell)$ are the zeros of the radicand--the classical turning points. Equation (1) defines the function $n(E, \ell)$ explicitly, which is the inverse function of $E(n, \ell)$.

The function $A(E, \ell)$ is defined by

$$A(E, \ell) \equiv \int_{E_{\min}}^E dE' \pi [n(E', \ell) + \frac{1}{2}] / (E - E')^{\frac{1}{2}}, \quad (2)$$

where E_{\min} is that value of E for which $n(E, \ell) = -\frac{1}{2}$. Equation (1) is substituted into Equation (2), and upon interchanging the order of integrations and using the integral relations

$$\int_a^b dx \left(\frac{x-a}{b-x}\right)^{\frac{1}{2}} = \int_a^b dx \left(\frac{b-x}{x-a}\right)^{\frac{1}{2}} = \frac{\pi}{2} (b-a) \quad (3)$$

one finds that

$$A(E, \ell) = \frac{\pi}{2} \left(\frac{2\mu}{n^2}\right)^{\frac{1}{2}} \int_{r_{<}}^{r_{>}} dr [E - V(r) - n^2 \ell^2 / 2\mu r^2] \quad (4)$$

Differentiation of Equation (4) gives

$$\frac{\partial A(E, \ell)}{\partial E} = \frac{\pi}{2} \left(\frac{2\mu}{n^2}\right)^{\frac{1}{2}} (r_{>} - r_{<}) \quad (5a)$$

$$\frac{\partial A(E, \ell)}{\partial \ell} = \frac{\pi}{2} \left(\frac{\hbar^2}{2\mu} \right)^{\frac{1}{2}} 2\ell \left(\frac{1}{r_{>}} - \frac{1}{r_{<}} \right) \quad (5b)$$

Since the function $A(E, \ell)$, as defined by Equation (2), is calculable from the experimental eigenvalues, the two equations for $r_{<}$ and $r_{>}$ in Equation (5) can be solved to obtain $r_{<}$ and $r_{>}$; the value of the potential at $r_{<}$ and $r_{>}$ is given by

$$V(r_{\leq}) = E - \hbar^2 \ell^2 / 2\mu r_{\leq}^2 \quad (6)$$

This is the standard RKR method.⁶

The above procedure has exploited the energy dependence of $n(E, \ell)$, using the fact that the dependence on E occurs in a manner such that integral transforms based on Equation (3) can be employed. One may also note, however, that the ℓ dependence occurs in a very similar manner. Proceeding analogously, therefore, the function $B(E, \ell)$ is defined by

$$B(E, \ell) \equiv \int_{\ell}^{\ell_{\max}} d\ell' 2\ell' \pi [n(E, \ell') + \frac{1}{2}] / (\ell'^2 - \ell^2)^{\frac{1}{2}} \quad (7)$$

where ℓ_{\max} is that value of ℓ for which $n(E, \ell) = -\frac{1}{2}$. Substituting Equation (1) into Equation (7), interchanging the order of integration, and using Equation (3) gives

$$B(E, \ell) = \frac{\pi}{2} \left(\frac{2\mu}{\hbar^2} \right) \int_{r_{<}}^{r_{>}} dr r [E - V(r) - \hbar^2 \ell^2 / 2\mu r^2] \quad (8)$$

Differentiation with respect to E and l , therefore, gives

$$\frac{\partial B(E, l)}{\partial E} = \frac{\pi}{4} \left(\frac{2\mu}{\hbar^2} \right) (r_{>}^2 - r_{<}^2) \quad (9a)$$

$$\frac{\partial B(E, l)}{\partial l} = \frac{\pi}{2} (2l) \ln (r_{>}/r_{<}) \quad (9b)$$

Since $B(E, l)$ is calculable via Equation (7) from the known eigenvalues, Equation (9) provides two equations by which $r_{<}$ and $r_{>}$ can be determined; the value of the potential at $r_{<}$ and $r_{>}$ is given by Equation (6).

Equations (7), (9) and (6), therefore, provide an inversion scheme analogous to the usual RKR scheme in Equations (2), (5) and (6). The principal disadvantage of Equation (9) is that one cannot solve these equations to obtain explicit expressions for $r_{<}$ and $r_{>}$ (due to the logarithms).

To summarize all of these inversion formulae it is useful to carry out the differentiations of $A(E, l)$ and $B(E, l)$ in Equations (2) and (7) explicitly;⁷ the resulting expressions are

$$r_{>} - r_{<} = \frac{2}{\pi} \left(\frac{\hbar^2}{2\mu} \right)^{\frac{1}{2}} \int_{E_{\min}}^E dE' \pi \frac{\partial n(E', l)}{\partial E'} / (E - E')^{\frac{1}{2}} \quad (10)$$

$$\frac{1}{r_{>}} - \frac{1}{r_{<}} = \frac{2}{\pi} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{1}{2}} \frac{1}{2l} \int_{E_{\min}}^E dE' \pi \frac{\partial n(E', l)}{\partial l} / (E - E')^{\frac{1}{2}} \quad (11)$$

$$r_{>}^2 - r_{<}^2 = \frac{4}{\pi} \left(\frac{\hbar^2}{2} \right) \int_{\ell}^{\ell_{\max}} d\ell' \frac{2\ell' \pi \frac{\partial n(E, \ell')}{\partial E}}{(\ell'^2 - \ell^2)^{\frac{1}{2}}} \quad (12)$$

$$\ln(r_{>}/r_{<}) = -\frac{2}{\pi} \int_{\ell}^{\ell_{\max}} d\ell' \frac{\pi \frac{\partial n(E, \ell')}{\partial \ell'}}{(\ell'^2 - \ell^2)^{\frac{1}{2}}}, \quad (13)$$

where $r_{\leq} = r_{\leq}(E, \ell)$; the value of the potential at r_{\leq} is given by Equation (6).

Any two of the four equations, Equation (10)-(13), may be used in conjunction with Equation (6) to provide an inversion scheme. For bound-state problems there is no apparent reason why any pair of equations should be easier to use than the usual RKR pair [Equations (10) and (11)]. Equations (12) and (13) do give alternate inversion relations, however, which may be of use in some situations.

III. Inversion Relations for Potential Scattering

The experimental observable in an elastic scattering experiment is the cross section $\sigma(\theta, E)$ --the differential cross section (or angular distribution) at relative collision energy E . Inversion schemes, however, invariably start with the scattering phase shifts $\eta(E, \ell)$ as a function of orbital angular momentum ℓ and collision energy E . The phase shifts can in principle be determined from the cross section,⁸⁻⁹ but it is certainly not a trivial aspect of the problem. Under semi-classical conditions the most promising approach is to attempt to

construct the classical deflection function from the differential cross section;^{1,2} the phase shift is easily obtained from the deflection function. This construction can be carried out at different energies, so that one can obtain the phase shift as a function of l and E . There are special circumstances in which particular phase shifts can be obtained more directly.¹⁰

We assume, therefore, that the phase shift $\eta(E, l)$ is known. One of the many equivalent forms of WKB approximation for η is

$$\eta(E, l) = \int_{r_0}^R dr \{2\mu[E - V(r)]/\hbar^2 - l^2/r^2\}^{\frac{1}{2}}$$

$$- \int_{l/k}^R dr \{2\mu E/\hbar^2 - l^2/r^2\}^{\frac{1}{2}}, \quad (14)$$

where $k = \sqrt{2\mu E/\hbar^2}$, $r_0 = r_0(E, l)$ is the classical turning point, and R is a large value of r (the limit $R \rightarrow \infty$ is implied). This expression for the phase shift, however, is quite similar to Equation (1) which given the radial (i.e., vibrational) quantum number for a potential well as a function of E and l . In fact,

$$\eta(E, l) = \pi[n(E, l) - n_0(E, l)], \quad (15)$$

where n is the radial quantum number for a potential well which is the actual effective potential $V(r) + \hbar^2 l^2/2\mu r^2$ plus an impenetrable vertical wall imposed at $r = R$. (This is reminiscent of "box normalization" for continuum states.¹¹) Likewise, n_0 is the "unperturbed" radial quantum

number for a potential well which is just the centrifugal potential $\hbar^2 l^2 / 2\mu r^2$ plus the vertical wall at $r = R$. The phase shift, therefore is the shift (in units of π) in the radial quantum number caused by the potential $V(r)$.

Having observed this expression for the phase shift, the results of Section II can be applied directly. For $n(E, l)$ one has $r_< = r_0$, $r_> = R$, and for $n_0(E, l)$ $r_< = l/k$, $r_> = R$. In terms of the phase shift, therefore, the four inversion relations are

$$r_0 = l/k - \frac{2}{\pi} \left(\frac{\hbar^2}{2\mu} \right)^{\frac{1}{2}} \int_{E_{\min}}^0 dE' \pi \frac{\partial n(E', l)}{\partial E'} / (E - E')^{\frac{1}{2}} - \frac{2}{\pi} \left(\frac{\hbar^2}{2\mu} \right)^{\frac{1}{2}} \int_0^E dE' \frac{\partial \eta(E', l)}{\partial E'} / (E - E')^{\frac{1}{2}} \quad (16)$$

$$\frac{1}{r_0} = k/l - \frac{2}{\pi} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{1}{2}} \frac{1}{2l} \int_{E_{\min}}^0 dE' \pi \frac{\partial n(E', l)}{\partial l} / (E - E')^{\frac{1}{2}} - \frac{2}{\pi} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{1}{2}} \frac{1}{2l} \int_0^E dE' \frac{\partial \eta(E', l)}{\partial l} / (E - E')^{\frac{1}{2}} \quad (17)$$

$$r_0^2 = (l/k)^2 - \frac{4}{\pi} \frac{\hbar^2}{2\mu} \int_l^\infty dl' 2l' \frac{\partial \eta(E, l')}{\partial E} / (l'^2 - l^2)^{\frac{1}{2}} \quad (18)$$

$$\ln r_0 = \ln(\ell/k) + \frac{2}{\pi} \int_{\ell}^{\infty} d\ell' \frac{\partial \eta(E, \ell')}{\partial \ell'} / (\ell'^2 - \ell^2)^{\frac{1}{2}} \quad (19)$$

where $r_0 = r_0(E, \ell)$ is the classical turning point; the value of the potential at r_0 is therefore

$$V(r_0) = E - \hbar^2 \ell^2 / 2\mu r_0^2 \quad (20)$$

Any one of the four equations, Equations (16)-(19), used in conjunction with Equation (20), provides an inversion scheme.

In Equations (16) and (17) it is seen that the bound-state eigenvalue function $n(E, \ell)$ is also required. (This is the same as in the quantum mechanical solution--inversion based on the energy dependence of the phase shift also requires information regarding the bound-states.¹² If the potential is purely repulsive, then the terms in Equations (16) and (17) involving the eigenvalue function are absent.

The only restrictions which must be imposed on the four equations have to do with avoiding the situation of three classical turning points;¹³ i.e., E and ℓ must be restricted so that the three turning point situation does not arise. For Equations (18) and (19) this means that the energy E must be greater than the maximum energy at which classical orbiting can occur; i.e., $E \geq E_{\text{orb}}$, where one can show² that

$$E_{\text{orb}} = \text{Max}_r [V(r) + \frac{1}{2} r V'(r)]. \quad (21)$$

For equations (16) and (17) the requirement is that the value of ℓ be such that the effective potential $V(r) + \hbar^2 \ell^2 / 2\mu r^2$ does not possess a local maximum. This is achieved by requiring either that $\ell = 0$, or

that $l \geq l_{\text{orb}}$, where one can show that l_{orb} (the maximum value of l for which classical orbiting is possible) is given by

$$l_{\text{orb}}^2 = \frac{2\mu}{\hbar^2} \frac{1}{2} \cdot \text{Max}_r [r^3 V'(r)] \quad (22)$$

Two of the four equations will be recognized as previously known results; Equation (19) is Firsov's formula,¹⁴ and the $l = 0$ version of Equation (16) has been given previously by Miller.² Equations (17) and (18) are new inversion relations for the phase shift.

As an example of how these formulae may be used, consider Equation (17) for the case that the potential is purely repulsive (so that the bound-state term is absent) and with $l = 0$. Thus

$$\frac{1}{r_0} = \lim_{l \rightarrow 0} \frac{1}{l} \left[k - \frac{1}{2\pi} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{1}{2}} \int_0^E dE' \theta(E', l) / (E-E')^{\frac{1}{2}} \right] \quad (23)$$

where we have used the fact that the deflection function $\theta(E, l)$ is related to the phase shift by

$$\theta(E, l) \equiv 2 \partial \eta(E, l) / \partial l .$$

It is easy to show that the expression in square brackets in Equation (23) goes to zero as $l \rightarrow 0$, so that L'Hospital's rule is applicable; thus

$$\frac{1}{r_0} = - \frac{1}{2\pi} \left(\frac{2\mu}{\hbar^2} \right)^{\frac{1}{2}} \int_0^E dE' \left. \frac{\partial \theta(E', l)}{\partial l} \right|_{l=0} / (E-E')^{\frac{1}{2}} . \quad (24)$$

The deflection function at $l = 0$, however, is closely related to the differential cross section at $\theta = \pi$:

$$\sigma(\pi, E) = \frac{1}{k^2} \left[\frac{\partial \Theta(E, \ell)}{\partial \ell} \Big|_{\ell=0} \right]^{-2},$$

or

$$\frac{\partial \Theta(E, \ell)}{\partial \ell} \Big|_{\ell=0} = -1 / k\sigma(\pi, E)^{\frac{1}{2}}. \quad (25)$$

Substituting Equation (25) into Equation (24) gives

$$\frac{1}{r_0} = \frac{1}{2\pi} \int_0^E dE' [\sigma(\pi, E') E' (E-E')]^{\frac{1}{2}},$$

and the value of the potential at r_0 is

$$V(r_0) = E.$$

These two equations can be combined to give the final expression

$$r(V) = 2\pi \int_0^V dE' [\sigma(\pi, E') E' (V-E')]^{-\frac{1}{2}}; \quad (26)$$

This gives $r(V)$ explicitly, the inverse function of which is $V(r)$. The potential is obtained, therefore, in terms of the energy dependence of the cross section for back scattering. A simple example for which Equation (26) can be checked is the repulsive Coulomb potential, $V(r) = 1/r$; the cross section for back scattering in this case is $\sigma(\pi, E) = 1/(4E)^2$.

IV. Other Applications

All of the above WKB inversion relations are based on the fact that it is possible to obtain phase integrals experimentally. In Section II

the eigenvalue function $n(E, \ell)$ is recognized as a phase integral, and in Section III the phase shift $\eta(E, \ell)$ is similarly identified as such. The various integral transforms of the known phase integrals permit the determination of the classical turning points and thus the value of r at which the potential has a definite value.

There are other situations in which phase integrals are obtainable experimentally and on which inversion schemes utilizing Equations (10)-(13) can be devised. Any time interference features are observed it is possible to determine the E and/or ℓ dependence of the pertinent phase integral; the phase integral is the phase of the oscillatory structure.

a. Franck-Condon Transitions

Processes in molecular dynamics which involve electronic transitions (such as absorption and emission of radiation, predissociation, and molecular autoionization) are usually "Franck-Condon transitions", meaning that the electronic rearrangement takes place essentially instantaneously with regard to nuclear motion. The relative intensity of such transitions is the product of a slowly varying function and a Franck-Condon factor (the overlap of the initial and final nuclear wavefunctions). Measurement of these relative intensities is therefore a measurement of the Franck-Condon factor.

The fact which makes an inversion scheme possible is that the Franck-Condon factor is intimately related to a phase integral; the phase integral in this case is associated with a potential well formed by the intersection of the initial and final potential curves.¹⁵ Child¹⁶ has utilized the energy dependence of this "Franck-Condon phase integral", through Equation (10) of Section II, to devise an inversion scheme for

Franck-Condon data obtained from predissociation intensities. If the dependence of the Franck-Condon factor on rotational quantum number is also determined, then one can also employ Equation (11), say, to determine both $r_{<}$ and $r_{>}$; if the dependence on vibrational quantum number is all that is known, it is only possible to use Equation (10) so that it is necessary to assume that either $r_{<}$ or $r_{>}$ is known in order to determine the other.

b. Curve Crossing Probability

In the semiclassical treatment¹⁷ of electronic transitions in atom-atom collisions which take place via a crossing of the two potential curves, the transition probability is the product of a slowly varying factor and an oscillatory factor. The phase of the oscillatory factor is a phase integral; more specifically, it is the difference in phase integrals on the initial and final potential curves from their respective classical turning points to the crossing point. If the E and l dependence of this phase integral can be extracted from the differential and/or total cross section for the electronic transition, then the inversion formulae of Section II can be utilized to construct the two potentials involved. If one of the potentials is known, then it would be possible to determine the other by knowing either the E -dependence or the l -dependence of the phase integral.

V. Conclusions

Except for the bound-state situation for which the experimental data are the vibrational-rotational eigenvalues, the most difficult aspect of inversion is the extraction of the E and l dependence of the pertinent phase integral from the experimental data (cross sections,

Franck-Condon factors, transition probabilities, etc.). To the extent to which this can be accomplished, inversion schemes based on some, or all of Equations (10)-(13) can be readily devised.

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 5. For simplicity of presentation we write l^2 for the square of angular momentum rather than $l(l+1)$ or $(l+\frac{1}{2})^2$; for the bound-state situation in Section II $l(l+1)$ is preferable, while it is customary to use $(l+\frac{1}{2})^2$ for scattering applications as in Section III. The formulae can be easily modified for either situation.
 6. For normal RKR applications it is useful to integrate Equation (2) by parts, so that $A(E, l)$ can be calculated by

$$A(E, l) = 2\pi \int_{-\frac{1}{2}}^{n(E, l)} dn [E - E(n, l)]^{\frac{1}{2}}$$
 7. To differentiate Equation (2) with respect to E and Equation (7) with respect to l , it is necessary first to integrate by parts and then differentiate.
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