Separation of Sets of Variables in Quantum Mechanics*

R. A. Marcus†

Departments of Chemistry
Brookhaven National Laboratory, Upton, New York
Polytechnic Institute of Brooklyn, Brooklyn, New York

Abstract

Separation of the Schrödinger equation for molecular dynamics into sets of variables can sometimes be performed when separation into individual variables is neither possible nor for certain purposes necessary. Sufficient conditions for such a separation are derived. They are the same as those found by Stäckel for the corresponding Hamilton-Jacobi problem, with an additional one which is the analog of the Robertson condition for one-dimensional sets.

Expressions are also derived for operators whose eigenvalues are the separation constants. They provide a variational property for these constants. For use in aperiodic problems an expression is obtained for the probability current in curvilinear coordinates in an invariant form. Application of these results to reaction rate theory is made elsewhere.

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†Visiting Senior Scientist, B.N.L. Present address: Polytechnic Institute of Brooklyn. This research was supported in part by a fellowship from the Alfred P. Sloan Foundation.
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Introduction

In 1891 Stackel obtained the necessary and sufficient conditions for separation of variables in the Hamilton-Jacobi equation, separating a partial differential equation for a system of n degrees of freedom into n ordinary differential equations.¹ Later, Robertson extended these results to the n-dimensional Schrödinger equation, obtaining conditions the same as those found by Stackel, plus one additional one.² The differential geometric implication of this last condition has been described by Eisenhart.³

In 1897 Stackel generalized his earlier work, by considering the conditions for separation of the Hamilton-Jacobi equation into sets of variables.⁴ His results reduced to those obtained previously¹ when each set consisted of only one coordinate. In the present paper, this result is extended to the n-dimensional Schrödinger equation, using arguments paralleling those employed by Robertson and by Stackel. An application to reaction rate theory is given elsewhere.⁵

In a subsequent section an expression for the probability current in curvilinear coordinates is derived by using the standard expression for the gradient in tensor calculus. (No separation of variables is assumed.) The expression has application to aperiodic problems. In a concluding section of the paper operators are formed whose eigenvalues are the separation constants. A variational property of these constants is then derived for use in approximations.
Derivation of Some Conditions for Separation.

The n-dimensional Schrödinger equation has the form (1).  

\[ \sum_{r,s=1}^{n} \frac{1}{\sqrt{g}} \frac{\partial}{\partial q_r} \left( \sqrt{g} \ g^{rs} \ \frac{\partial \psi}{\partial q_s} \right) + k^2 (\alpha_1 - V) \psi = 0 \]  

where \( k^2 \) equals \( \frac{2}{\hbar^2} \), \( \alpha_1 \) is the energy \( E \), \( V \) is the potential energy and \( \psi \) the wave function for the entire system. \( g^{rs} \) is reciprocal to \( g_{rs} \). The \( g^{rs} \) appear in the fundamental line element \( ds \) in a space having the \( q^r \) as generalized coordinates and are defined by (2b). 

\[ ds^2 = \sum_{r,s=1}^{n} g^{rs} \ dq_r \ dq_s \]  

If the coordinates \( q^r \) are the ordinary Cartesian coordinates \( x^r \) then \( g_{rs} \) equals \( m_i \delta_{rs} \), the mass of the atom whose coordinates include this \( x^r \) and \( \delta_{rs} \) is the Kronecker delta function. If the coordinates \( q^r \) are any other ones, corresponding \( g_{rs} \) are computed from the expression,

\[ g_{rs} = \sum_{i=1}^{n} m_i \ \frac{\partial x^1}{\partial q^r} \ \frac{\partial x^1}{\partial q^s} ; \quad g^{rs} = \sum_{i=1}^{n} \ m_i \ \frac{\partial q^r}{\partial x^1} \ \frac{\partial q^s}{\partial x^1} \]  

For example, if the \( q^r \) are mass-weighted Cartesian coordinates, i.e. if they equal \( \sqrt{m_r} \ x^r \), then \( g_{rs} \) equals \( \delta_{rs} \).

Robertson considered systems having orthogonal coordinates \( (g^{rs} = 0 \text{ if } r \neq s) \). In generalizing to sets of coordinates, we consider (as did Stäckel in 1897) systems for which any coordinates belonging to different sets are
orthogonal, and so those for which \( g_{rs} \) vanishes when \( r \) and \( s \) belong to different sets.

Denoting the \( \mu \)'th set by an index \( \mu \), let it contain \( h \) coordinates and let there be \( m \) sets. Then,

\[
\sum_{\mu=1}^{m} h_{\mu} = n
\]

The coordinates in the \( \mu \)'th set will be denoted by \( q_{\mu}^{i} \) \((i = 1 \text{ to } h_{\mu})\) and will be referred to as set \( \mu \). The Schrödinger equation (1) then becomes

\[
\frac{1}{\sqrt{g}} \sum_{\mu=1}^{m} h_{\mu} \sum_{i,j=1}^{h} \sqrt{g} g^{\mu i j} \frac{\partial \psi}{\partial q_{\mu}^{i}} + k^{2} (\alpha_{1} - V) \psi = 0 \tag{2}
\]

To find some conditions for the separation we shall impose condition (3) on the \( g^{\mu i j} \). Eventually conditions will be found in which (3) plays a role. They will be shown later to be sufficient to effect separation rather than being necessary:

\[
g^{\mu i j} \sqrt{g} = f^{\mu i j} a_{\mu} \tag{3}
\]

where \( f^{\mu i j} \) depends only on set \( \mu \) and where \( a_{\mu} \) depends only on coordinates in the remaining \( m-1 \) sets. Upon introducing (3) and (4), where \( \psi_{\mu} \) depends only on set \( \mu \), (2) yields (5).

\[
\psi = \prod_{\mu=1}^{m} \psi_{\mu} \tag{4}
\]

(Problems in which there are symmetry or antisymmetry conditions on
\[ \frac{1}{\sqrt{g}} \sum_{\mu} a_{\mu} \psi_{1} \psi_{u} \frac{\partial^2}{\partial q^{1}_{\mu}} f \frac{\partial^2}{\partial q^{1}_{\mu}} = k^2 \left( a_{1} - V \right) = 0 \] (5)

If Eq. (5) is separated into \( m \) partial differential equations, one for each set \( \psi_{\mu} \), there will be \( m - 1 \) separation constants, \( a_{2} \) to \( a_{m} \). Each \( \psi_{\mu} \) will depend on \( a_{1} \) to \( a_{m} \) and so (5) can be regarded as an identity in \( a_{1} \) to \( a_{m} \); i.e., it is satisfied for arbitrary values of \( a_{1}, \ldots, a_{m} \).

It can be differentiated with respect to any of these \( a_{\nu} \), noting that \( V \) is of course independent of the \( a_{\nu} \)'s. One so obtains \( m \) equations:

\[ \frac{1}{\sqrt{g}} \sum_{\mu} a_{\mu} W_{\mu \nu} = \delta_{1 \nu} \] (6)

where \( W_{\mu \nu} \) is a function only of the coordinates in the \( \mu \)'th set and of the \( a_{\nu} \)’s:

\[ W_{\mu \nu} = - \frac{1}{k^2} \frac{\partial}{\partial \alpha_{\nu}} \frac{1}{m} \frac{\partial}{\partial q^{1}_{\mu}} f \frac{\partial^2}{\partial q^{1}_{\mu}} \frac{\partial \psi_{\mu}}{\partial q^{1}_{\mu}} \] (7)

It must be possible to find a value of \( (a_{1}, \ldots, a_{m}) \), say \( (a_{1}^{1}, \ldots, a_{m}^{1}) \), such that \( \det W_{\mu \nu} \) in Eq. (6) does not vanish. (Otherwise, \( \psi \) would depend on less than \( m \) constants \( a_{\nu} \); cf. Appendix I.) Let the corresponding value of \( W_{\mu \nu} \) be denoted by \( \hat{W}_{\mu \nu} \). It depends no longer on \( (a_{1}, \ldots, a_{n}) \). For this \( \hat{a} = a^{1} \), the functions conjugate to these \( \hat{\psi}_{\mu \nu}, \hat{\psi}_{\mu \nu} \), exist since the determinant of the \( \hat{\psi}_{\mu \nu}, \hat{\psi}_{\mu \nu} \), is non-zero, \( \hat{w} \) may
write
\[ \sum_{\mu=1}^{m} \phi'^{\mu} \nabla_{\mu} = \delta_{\nu} \lambda. \] (8)

Comparison with (6) then shows that
\[ \phi'^{\mu} = \alpha \sqrt{g} \] (9)

According to (8) \( \phi'^{\mu} \) is the cofactor of \( \phi_{\mu} \) in \( \phi' \). Since each \( \phi'^{\mu} \) depends only on the coordinates in the \( \mu \)'th row, the cofactor \( \phi'^{\mu} \) must be independent of them, as is \( \alpha \) by definition. From (9), it then follows that \( \phi' \sqrt{g} \) is independent of the coordinates of the \( \mu \)'th set. Since this independence holds for all \( \mu \) we have:
\[ \phi' \sqrt{g} = K, \text{ a constant} \] (I)

From (3) and (9) we also have
\[ g^{\mu \nu}_{ij} = \phi'^{\mu} \phi'^{\nu} \] (II)

Finally, Eq. (5) can be written as in (10), using (8) and (9).
\[ V = \sum_{\mu=1}^{m} \phi'^{\mu} \left( a_{\mu} \phi'^{\mu} \frac{1}{k^2} \frac{1}{\psi_{\mu}} \sum_{i,j=1}^{n} \frac{3}{\delta \phi_{ij}^{\mu}} \phi'^{\mu} \frac{\partial \phi_{ij}^{\mu}}{\delta \phi_{ij}^{\mu}} \right) \] (10)

The r.h.s. of (10) is only apparently a function of the \( \alpha \)'s. Like \( V \), it must actually be independent of them, and so is unchanged when the \((\alpha_1, \ldots, \alpha_n)\) is replaced by \((\alpha_0, \ldots, \alpha_0)\).
The corresponding function in parentheses is a function of set \( \mu \) alone and will be denoted by \( X_\mu \). Thus, a third condition for the separation of variables is:

\[
V = \sum_\mu \phi^\mu_1 \cdot X_\mu \quad (\text{III}')
\]

**Conditions (I') to (III') are Sufficient**

Conditions (I') to (III') are also sufficient for separation of the variables into the \( m \) sets:

Inserting these conditions into the Schrödinger equation (2), noting that \( \phi^\mu_1 \) is independent of set \( \mu \), using (8) one obtains

\[
\sum_\mu \phi^\mu_1 \cdot X_\mu = 0 \quad (11)
\]

where

\[
\psi_\mu = \frac{h_\mu}{\psi_{\mu}} \sum_{i,j} \frac{\delta}{\delta q_{ij}} \phi^\mu_i \cdot j \cdot Y_i + k^2 (\alpha \cdot \phi^\mu_1 - X_\mu) \quad (12)
\]

Consider any specified value of all the coordinates in the system. \( (Y_1, ..., Y_m) \) can then be regarded as a vector in an \( m \)-dimensional space, with components \( Y_1, ..., Y_m \). This vector is orthogonal to another vector \((\phi^\mu_1, ..., \phi^\mu_m)\) in this same space.
However, there are already \( m-1 \) linearly independent vectors orthogonal to \((\phi^{'1},...,\phi^{'m})\), namely \((\phi_{1},...,\phi_{m})\)
where \( \lambda = 2 \) to \( m \). It follows that \((Y_{1},...,Y_{m})\) must be a linear combination of them.

I.e., \( Y_{\mu} = -k^{2} \sum_{\nu=2}^{m} \alpha_{\nu} \phi_{\mu}^{\nu} \) \hspace{1cm} (13)

where the \( \alpha_{\nu} \) are constants. Eq.(13) holds for any set of specified values of all the coordinates, and hence over all configuration space. Eqs. (12) and (13) yield the separated equations:

\[
j_{\mu} \sum_{i,j=1}^{n} \frac{\partial}{\partial q_{\mu}} r^{\nu i} q_{\mu} \frac{\partial}{\partial q_{\nu}} q_{\mu} + k^{2} \left( \sum_{\nu=1}^{m} \alpha_{\nu} \phi_{\mu}^{\nu} - x_{\mu} \right) \psi_{\mu} = 0 \hspace{1cm} (14)
\]

In summary, one sees that given \( m^{2} \) quantities, \( \phi_{\mu \nu} \) such that each is a function only of the set of variables described by the first index and such that the product of their determinant with \( \sqrt{g} \) is a constant, then a separation of variables into sets of variables can be effected when conditions \((II)'\) and \((III)'\) are also fulfilled.

**Comparison with Stäckel and Robertson**

Stäckel found that conditions \((II)'\) and \((III)'\) alone sufficed for separation of the Hamilton-Jacobi equation. \((I)'\) is the analogue of the additional one found by Robertson for the case where each subspace \( \mu \) is one-dimensional.

For comparison with Robertson's results and for application
it is convenient to define new quantities $\phi_{\mu\nu}$, $f_i^{\mu\nu j}$, 
$X_\mu$ and $\phi^{\mu\nu}$:

$$
\phi_{\mu\nu} = f_{\mu\nu}' / f_{\mu}', \quad f_i^{\mu\nu j} = f_i^{\mu\nu j}/k^{1/m} 
$$

$$
X_\mu = X_\mu'/ f_\mu', \quad \phi_{\mu\nu} = \phi_{\mu\nu}' / f_\mu'
$$

where $f'$ is the $h_\mu$th root of an $h_\mu x_\mu$ determinant,

$$
det_{\mu, \nu} f^{\mu\nu j}_{i, j=1}.
$$

From (15) $\phi$ equals $\phi'/f_{\mu}'$. We introduce

$$
f_{\mu}:
$$

$$
f_{\mu} = \frac{h_{\mu}}{(det_{i, j=1} f_i^{\mu\nu j})^{1/h_{\mu}}}
$$

which equals $f_i'^{\mu}/k^{1/m}$. The quantities $f_i^{\mu\nu j}$, $f_{\mu}$ and $\phi_{\mu\nu}$
are again functions only of the $\mu$th set of variables. From (8) and

$$
(\sum_{\mu=1}^{N} \phi_{\mu\nu}' \phi_{\mu\nu}) = \delta_{\mu\nu}
$$

With these quantities, conditions (I) to (III) become the following conditions on the $e_{rs}^q$ and on $V$.

$$
\phi/\sqrt{g} = 1/ \sum_{\mu=1}^{m} f_{\mu} \quad (I)
$$

$$
\phi_{\mu}' (\sum_{i, j=1}^{m} g_i^{\mu\nu j})^{1/h_{\mu}} = \phi_{\mu} \quad (II)
$$

$$
V = \sum_{\mu=1}^{m} \phi_{\mu} X_\mu \quad (III)
$$

The separated equations become:

$$
\frac{1}{f_{\mu}} \sum_{i, j=1}^{m} \frac{\partial}{\partial q_i^{\mu\nu}} f_i^{\mu\nu j} \frac{\partial}{\partial q_j^{\mu\nu}} \psi_{\mu} + k^2 (\sum_{\mu=1}^{m} a_{\mu} \phi_{\mu\nu} - X_\mu \phi_{\mu\nu} = 0 \quad (17)
$$
where

\[
\begin{align*}
I_{j}^{i} & = g_{j}^{i} f_{j}^{i} / \left( \text{det} g_{i}^{j} \right)^{1/2}
\end{align*}
\]

In the special case that all the subspaces \( \mu \) are one-dimensional there is only one \( I_{j}^{i} \) for each \( \mu \), and so the latter equals its determinant \( f_{\mu} \). There is also only one \( g_{j}^{i} \) for each \( \mu \), which then equals its determinant. The conditions and the separated equations then reduce to those obtained by Robertson.

Given a set of coordinates which permit a separation into sets of variables and given some method (not specified) for determining the Stäckel coefficients \( \Phi_{\mu} \), Equation (I) provides the values for the \( f_{\mu} \)'s: Each \( f_{\mu} \) is the factor in \( \rho / \sqrt{g} \) which depends only on set \( \mu \). Equation (18) is then used to determine the \( I_{j}^{i} \)'s.

The separated equations are given by (17)

The problems of determining the systems of subspaces which permit separation variables and determining the Stäckel coefficients remain as separate problems. Eisenhart solved the one dimensional analogs of conditions (I) to (III) and determined thereby all the coordinate systems in \( n \)-dimensions which permit separation of the Schrödinger equation into \( n \) 1-dimensional equations. He has tabulated the Stäckel coefficients for \( n = 3 \) but not for larger \( n \). Presumably those for larger \( n \) can be derived from various results in his paper. Then again, a study analogous to Eisenhart's but
devised for several-dimensional sets rather than for purely one-dimensional ones would be of interest here.

To illustrate for later use how a common case falls within the formalism embodied in Eqs. (I) to (III), (17) and (18), we consider in Appendix II the separation of rotation from vibration in a diatomic molecule.

**Probability Current in Curvilinear Coordinates**

Usually, literature expressions for the probability current across a surface are given for Cartesian or spherical polar coordinates, sometimes mass-weighted, more often not. By using an expression for the current in an invariant form and then introducing the standard form for \( \mathbf{v} \) in Riemannian geometry one may obtain the current in curvilinear coordinates. The result, given by Eq. (23), reduces to (24) when the surface being crossed is a coordinate hypersurface. The result is then used to obtain an expression for the transmission coefficient.

It will be recalled that from the time dependent Schrodinger equation, \( H \psi = (\hbar/2m) \partial \psi / \partial t \), an equation of continuity (19) can be derived, where the probability density \( \rho \) is \( \psi^* \psi \) and where \( \mathbf{I} \) is a vector defined by (20).
\[ \frac{\partial \mathbf{A}}{\partial t} + \nabla \cdot \mathbf{I} \approx 0 \]  
(19)

\[ I = \frac{n}{2i} (\psi^* \nabla \psi - \psi \nabla \psi^*) \]  
(20)

According to Green's theorem in n-dimensions, \( \nabla \cdot \mathbf{I} \) integrated over some volume \( V \) equals \( I \cdot \mathbf{n} \) integrated over the area \( S \) enclosing \( V \), \( \mathbf{n} \) being the unit outward drawn vector normal to \( S \). Because of the probability interpretation of \( \rho \) it then follows from (19) in the standard way that \( J \), the probability current through \( S \), is given by (21). It is, of course, a scalar.

\[ J = \int_S I \cdot \mathbf{n} \, d\mathbf{S} \]  
(21)

where \( d\mathbf{S} \) is the area element of \( S \).

The covariant and contravariant components of \( \nabla \) along the coordinate curve \( q^j \) are \( \partial / \partial q^j \) and \( \sum_{i=1}^n g^{ij} \partial / \partial q^i \), respectively. The corresponding components of the vector \( \mathbf{I} \) are therefore seen from (20) to be:

\[ I^i_j = \frac{n}{2i} \left[ (\psi^* \frac{\partial \psi}{\partial q^j} - \psi \frac{\partial \psi^*}{\partial q^j}) \right] ; \quad I_j^i = \sum_{i=1}^n g^{ij} I_i \]  
(22)

Inasmuch as the inner product \( I \cdot \mathbf{J} \) is \( \sum_{j=1}^n I^i_j \mathbf{J}^j \) (and \( \sum_{i=1}^n I^i_j \mathbf{J}^i_j \)), Equation (21) is equivalent to:

\[ J = \int_S \frac{n}{j \mathbf{J}^i_j} d\mathbf{S} \]  
(23)

Although \( S \) is a closed surface, it often happens that if one considers two bounded portions of \( S \), joined by some connecting surface, and lets the two bounded regions in-
crease in size indefinitely, the contributions of the current through the connecting portions ultimately becomes negligible. For example, this occurs when \( \Psi \) is square integrable over the first two infinite regions. If \( \Psi \) describes a wave packet and we remove one of the two remaining surfaces to infinity only the remaining surface contributes to \( J \) in any finite time.

With these remarks as preliminary we consider the case that \( S \) represents a single \( q^i \)-coordinate hypersurface, \( S_N \), over which \( \Psi \) is square integrable. Only the \( V_N \) term in (23) does not vanish and, as discussed in Appendix III, \( V_N \) equals
\[
\sqrt{g} \frac{1}{iN} dq^i.
\]
The probability current \( J \) through \( S_N \) is therefore:
\[
J = \int_{S_N} I_N \sqrt{g} \frac{1}{iN} dq^i \tag{24}
\]
where \( I_N \) is given by (22).

**Transmission Coefficient**

As in the Cartesian case, we take \( J \) to be the probability current when the behavior of the wave packet is approximated by that of an infinite wave train (i.e. by an improper eigenfunction). The transmission coefficient is defined to be the ratio of transmitted to incident probability current.

Let the wave function be given by (4), where \( \frac{1}{\mu+N} \Psi \) is square integrable over the coordinate hypersurface \( S_N \). We consider an open coordinate curve \( q^N \) and note that for large values of \( q^N \), \( \Psi_N \) has the following asymptotic form. (Set \( N \) is now 1-dimensional.)
and where the region considered is one where \( \mathcal{K}_N \) is real. (For large \( q^N \) in the cases we have examined, \( f_N \) behaves as a power of \( q^N \).) Then the second two terms in (26) vanish asymptotically.

Solution of the Schrödinger equation subject to the boundary conditions (25) permits the determination of \( T \). Using (24), one also finds:

\[
J_{\text{trans}} = |T|^2 \mathcal{S}, \quad J_{\text{inc}} = \mathcal{J}, \quad J_{\text{inc}} + J_{\text{refl}} = (1 - |R|^2) \mathcal{S}
\]

where

\[
\mathcal{S} = \frac{1}{N} \int \phi \phi^{N_1} \mathcal{F}(|\phi|^2 f \, dq^N)
\]

By definition, we have:

\[
\mathcal{K} = J_{\text{trans}} / J_{\text{inc}} = |T|^2
\]

Inasmuch as \( \phi \phi^{N_1} \) and the remaining factors in (28) are independent of \( q^N \) (\( \phi \phi^{N_1} \) is the cofactor of \( \phi_{N_1} \) in \( \phi \)), \( \mathcal{S} \) is independent of \( q^N \), and so \( J_{\text{inc}} \) and \( J_{\text{trans}} \) are well defined. \( \mathcal{K} \) depends only on the constants of the motion. Conservation of \( J \) leads to \( |T|^2 \) being equal to \( 1 - |R|^2 \).

The quantity \( \mathcal{S} \) appears not only in (28) but elsewhere, as in Eq. (42) for \( k=1 \). Normalization of wave functions of incident particles for which \( \psi \) is not square integrable over \( S_N \) is common in the literature, the normalization being to unit current density. In the present case of \( \psi \)'square integrable over \( S_N \) a normalization to unit current would seem appropriate. We therefore set \( \mathcal{S} = 1 \).
Operators and a Variational Property for the $\alpha_\nu$

For possible applications in approximations, we obtain below the Hermitian operators for which the $\alpha_\nu$ are eigenvalues, and obtain thereby a stationary expression for the $\alpha_\nu$.

(a) Case of discrete spectrum for $\alpha_\nu$'s

Multiplying the $\mu$th equation (17) by $\phi^{\mu\lambda}_{\nu} \sum_j \psi_j$, summing over $\mu$, introducing (18), and finally replacing $\lambda$ by $\nu$, one obtains:

$$H(\nu) \psi = \alpha_\nu \psi$$

where

$$H(\nu) = \sum_{\mu=1}^{m} \left[ \frac{\hbar^2}{2m} \frac{1}{\sqrt{g}} \phi^{\mu\nu}_{\nu} \frac{\partial}{\partial q^{\mu\nu}_{\nu}} + \phi^{\mu\nu}_{\nu} \lambda_{\mu} \right]$$

When $\nu$ is 1, $H(\nu)$ is the Hamiltonian.

Defining an inner product (32), where $\psi_A$ and $\psi_B$ are any acceptable wave functions, and $d\lambda$ denotes $\int dq^{\mu\nu}_{\nu}$, one obtains (33) from (30):

$$(\psi_A, \psi_B) = \int \psi_A \psi_B \sqrt{g} \sum_{\mu=1}^{m} d\lambda^{\mu\nu}_{\nu}$$

$$\alpha_\nu = (\psi, H(\nu) \psi)/(\psi, \psi)$$

The operator $H(\nu)$ is Hermitian: Inasmuch as $\phi^{\mu\nu}/\phi^{\mu\nu}_{\nu}$ equals $\phi^{\mu\nu}_{\nu}/\phi^{\mu\nu}$ and both $\phi^{\mu\nu}$ and $\phi^{\mu\nu}_{\nu}$ are independent of the coordinates of set $\mu$, integration by parts shows that:

$$(\psi_A, H(\nu) \psi_B) = (H(\nu) \psi_A, \psi_B).$$

Expression (33) has the desired variational property:
it is stationary with respect to variations in $\psi$ for in the standard way one finds with the aid of (29):

$$
\delta \alpha, \nu = \left( \delta \psi, (H(1)) \psi - \frac{\langle \psi, H(\nu) \psi \rangle}{\langle \psi, \psi \rangle} \right) + \text{complex conjugate}
$$

Using (30) and (32) one sees that $\delta \alpha, \nu$ vanishes. Setting $\delta \alpha, \nu = 0$ (35) becomes an equation which may be solved for any variational parameters in $\psi$, remembering that these occur in the $m$ equations, $\nu = 1, 2, \ldots, m$.

We note that although $H(1)$ is defined whether the Schrödinger equation is separable or not, the other $H(\nu)$ in (31) are defined for the separable case, for only then are $\phi, \mu$, and $\chi, \nu$ defined, or when $\sum \phi, \nu \chi, \mu$ vanishes.

(b) Continuous spectrum case, but all $\alpha, \nu$'s discrete if one $\alpha, \nu$ prescribed.

We consider the behavior in a range of $q^N$ where the coordinate $q^N$ can be treated classically. This is the typical situation at large values of $q^N$. Near this $q^N$, the equation (17) for $\mu = N$ may be replaced by the classical equation (36).

$$
\frac{1}{2} p_N^2 + x_N = \sum_{\nu = 1}^{m} \alpha, \nu \phi_N, \nu
$$

where $p_N$ is the momentum conjugate to $q^N$ (cf Appendix I of Ref. 5).

Let us prescribe the values of one $\alpha, \nu$, call it $\alpha_k$, and $q^N$. We seek a stationary expression for the remaining
Let $M^\mu \lambda$ be the algebraic complement of $q^\mu \lambda \ - q^\mu k$ in the determinant, $q$. ($\lambda \neq k$.) Then:

$$M^\mu \lambda = \phi (\phi^\mu \lambda \ - \phi^\mu k)$$

(37)

From (16) and (37) one deduces the property:

$$\sum_{\mu \neq N} M^\mu \lambda q^\mu p = \phi \phi^N k - \phi \phi^N \lambda \ - \phi \phi^N \lambda \ - \phi \phi^N \lambda$$

(38)

Multiplying the $\mu$'th equation (17) by $\frac{\Xi_j}{\mu \neq N} \phi_j$ $M^\mu \lambda \phi^N k$, summing over all $\mu$ but $N$, using (1), (2), (3), and (4) and the fact that $\frac{\Xi_j}{\mu \neq N} \phi_j$ and $q^\mu$ are independent of $q^\mu$, and finally replacing $\lambda$ by $\psi$, one obtains:

$$H_N(\psi) \psi' = \alpha \psi$$

(39)

where

$$\psi' = \frac{\Xi_j}{\mu \neq N} \psi_{\mu}$$

(40)

and

$$H_N(\psi) = \sum_{\mu \neq N} \frac{M^\mu \lambda}{\phi \phi^N k} \frac{2}{\Xi_j \phi \lambda} \sum_{i, j} \frac{\phi_i \mu j}{\phi \phi^N k} + \frac{\phi_j \mu j}{\phi \phi^N k} + \frac{\phi_j \mu j}{\phi \phi^N k} + \alpha_k \phi \phi^N k$$

(41)

Introduction of the abbreviation $(\cdot)$ defined in (42), where $\psi_A$ and $\psi_B$ are any two acceptable wave functions, multiplication of (39) by $\psi^* \phi^N k$ $\Xi_j \phi \lambda$ and integration over all $q^j$ but $q^N$ leads to (43).

$$(\psi_A, \psi_B) = \Xi \int \psi_A^* \psi_B \phi \phi^N k \Xi_j \phi \lambda dq^j$$

(42)

$$\alpha \psi = (\psi', H_N(\psi') \psi')_N/(\psi', \psi')_N$$

(43)

One can also show:

$$(\psi_A, H_N(\psi_B) \psi_B) = (H_N(\psi), \psi_A', \psi_B')_N$$

(44)
When the Stackel coefficients are real as they are in the systems discussed by Eisenhart and perhaps in all systems of interest in molecular dynamics ($g^{\tau\pi}$ is real), one can show from (42) and (43) that the complex conjugate of $\alpha_j$ equals $\alpha_j$, i.e., $\alpha_j$ is real.

Because of (44) and (39), expression (42) can then be shown to be stationary in $\alpha_j$ for variations in $\Psi''$. 

We have refrained from calling $(\psi_A', \psi_B')_{\Pi_k}$ an inner product (and $H_N(\psi)$ Hermitian), for we did not show its positivity when $\psi_A'$ equals $\psi_B'$. (It has the other properties of an inner product.) In some typical cases of interest this positivity is established in Appendix IV. However, regardless of the sign of $(\psi', \psi')_{\Pi_k}$, the $\alpha_j$ is real and (43) is an extremum with respect to variations in $\Psi$. 
Appendix I. Note on det $\psi_{\mu \nu}$ Not Vanishing Identically

Let $\rho_{\mu}$ denote

$$\frac{1}{\psi_{\mu}} \sum_{i,j=1}^{n} \frac{\partial}{\partial q_{\mu i}} \int_{0}^{1} \mu^{i} j \frac{\psi_{\mu j}}{\partial q_{\mu j}}$$

The $\rho_{\mu}$ are functions of the $\alpha_{\nu}$ and of the $q_{\mu i}$. The coordinates $q_{\mu i}$ are treated as parameters for our purposes.

If $\det \sum_{\mu=1}^{n} \frac{\rho_{\mu}}{\partial \alpha_{\nu}}$ vanished identically and if there were $m$ independent $\alpha_{\nu}$'s ($\alpha_{1}$ to $\alpha_{m}$) there would be a functional dependence between the $\rho_{\mu}$'s, a dependence which could depend parametrically on the $q_{i}$. However, such a dependence would introduce one between the $q_{i}$'s. (See below.)

But these are independent variables, so $\det \sum_{\mu=1}^{n} \frac{\rho_{\mu}}{\partial \alpha_{\nu}} \neq 0$.

To see the resulting dependence between the $q_{\mu i}$'s, mentioned above, we consider for brevity the case of two dimensions. Functional dependence, with the $q_{i}$ appearing as parameters, means that $F(\rho_{1}, \rho_{2}, q^{1}, q^{2}) = 0$ where $\rho_{1} = \rho_{1}(q^{1}, \alpha_{1}, \alpha_{2})$ and $\rho_{2} = \rho_{2}(q^{2}, \alpha_{1}, \alpha_{2})$ but where $\alpha_{1}$ and $\alpha_{2}$ do not appear otherwise in $F$. At fixed $q^{1}$ and $q^{2}$ it is impossible to vary $F$ holding $\rho_{1}$ fixed and impossible to vary it holding $\rho_{2}$ fixed. I.e., $(\frac{\partial F}{\partial \rho_{1}})_{\rho_{2}, q^{1}, q^{2}} = 0$ and $(\frac{\partial F}{\partial \rho_{2}})_{\rho_{1}, q^{1}, q^{2}} = 0$. We now note that differentiation of $F = 0$ with respect to $q^{1}$ yields:
\[
\frac{\partial F}{\partial p_1}\frac{d\rho_1}{dq^1} + \frac{\partial F}{\partial p_2}\frac{d\rho_2}{dq^1} + \frac{\partial F}{\partial q^1} + \frac{\partial F}{\partial q^2}\frac{dq^2}{dq^1} = 0
\]

But the first, second and fourth terms vanish, so \(\partial F/\partial q^1 = 0\). Similarly \(\partial F/\partial q^2 = 0\). The functional dependence now becomes \(F(p_1, p_2) = 0\). Introduction of the explicit dependence of \(\rho^1\) and \(\rho^2\) on \(q^1\) and \(\alpha^1\) then leads to a relation between \(q^1\) and \(q^2\) for any given \(\alpha_1\) and \(\alpha_2\), which is impossible since \(q^1\) and \(q^2\) are independent variables.
Appendix II. The Rotating-Vibrating Diatomic Molecule

As a simple illustration we consider the diatomic molecule, the results for which are also easily obtained by standard methods.

If \( r \) is the internuclear distance, \( \theta \) and \( \beta \) the angles defining the orientation of the molecular axis, and \( M \) the reduced mass, let \( \mu = 1 \) correspond to \( r \) (vibration) and \( \mu = 2 \) correspond to \( f(\theta, \beta) \) (rotation). Since \( M^{-1} \) appears in all the \( g_{\mu \nu} \)'s, we shall merely absorb it in the \( k^2 \), so \( k^2 \) becomes \( 2M/\hbar^2 \). From the Schrödinger equation for this system one finds

\[
g_{11} = g_{rr} = 1, \quad g_{12} = g_{\theta \theta} = r^2, \quad g_{22} = g_{\beta \beta} = (r^2 \sin^2 \theta)^{-1},
\]

\( g_{12} = 0 \), whence \( \sqrt{g} = r^2 \sin \theta \).

From these results one finds \( f_{12} = r^{-2}, f_{21} = \sin \theta, \phi = \sin \theta \). Hence,

\[
\phi = \sin \theta = \begin{vmatrix} \phi_{11} & r^{-2} \\ \phi_{21} & \sin \theta \end{vmatrix} \quad (A1)
\]

Recalling that \( \phi_{\mu \nu} \) is a function only of coordinates in set \( \mu \), a solution to (A1) is seen to be: \( \phi_{11} = 1, \phi_{21} = 0 \).

Since \( \phi/\sqrt{g} \) equals \( r^{-2} \), Eq. (III) is satisfied and one may write \( f_1 = r^2, f_2 = 1 \). Calculating the \( f^{\mu_1 \mu_2} \) from (18) and satisfying (II) by writing

\[
V(r, \theta, \beta) = X_1(r) + \frac{X_2(\theta, \beta)}{r^2 \sin \theta}, \quad (A2)
\]

the separated equations are:
\[
\frac{1}{r^2} \frac{d}{dr} \frac{1}{r^2} \frac{d}{dr} \psi_1 + \frac{2M}{\hbar^2} \left( \alpha_1 + \frac{\alpha_2}{r^2} - x_1 \right) \psi_1 = 0 \quad (A3)
\]

\[
\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial \psi_2}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi_2}{\partial \beta^2} + \frac{2M}{\hbar^2} \left( \alpha_2 - \frac{x_2}{\sin \theta} \right) \psi_2 = 0 \quad (A4)
\]

where

\[
\psi = \psi_1(r) \psi_2(\theta, \beta) \quad (A5)
\]

and where the second term in (A2) is the only allowed potential energy term arising from external forces for which the equation is still separable. When \( x_2 \) vanishes, the constant of the motion \( 2M \alpha_2 \) becomes the square of the total angular momentum. To further separate (A4) into \( \theta \) and \( \beta \) equations it would be necessary that \( x_2(\theta, \beta) \) be the sum of \( h_1(\theta) / \sin \theta \) and \( h_2(\beta) / \sin \theta \), where \( h_1(\theta) \) and \( h_2(\beta) \) are arbitrary.
Appendix III. Magnitude of the Area element

The area element $d\sigma$ of $S^N$ is $\sqrt{g_{NN}} \sum_{i+N}^{j+N} dq^i$; $d\sigma$ is
the "volume element" in $S^N$ and so equals $\sqrt{\text{det} g_{ij}} \sum_{i+j=N} dq^i$. (The
volume element contains the determinant of the coefficients $g_{ij}$ appearing
in the expression for the line element $ds$ on $S^N$ all $g_{ij}$ occur in the line
element except those for which $i$ or $j$ or both equal $N$.) Since the
indicated determinant is also the cofactor of $g_{NN}$ in $g$ it equals
$g_{NN}$ and the value cited for the area element follows.

A more instructive proof perhaps is obtained by noting
that $d\sigma$ equals the n-dimensional volume element $dS$ divided by $\delta$,
the perpendicular distance between $S^N$ and another $q^N$ coordinate
hypersurface for which $q^N$ differs by $dq^N$. If $\delta$ is a vector normal
to $S^N$ and having a length $\delta$ its contravariant component along $q^N$
must be equal to $dq^N$, by definition. Some manipulation then
shows that $\delta = dq^N/\sqrt{g_{NN}}$. The value cited for $d\sigma$ then follows.
(The manipulation is somewhat similar to that involved in showing
that a vector of unit length and normal to $S^N$ has a contravariant
component along $q^N$ equal to $\sqrt{g_{NN}}$.)

Appendix IV. The sign of \((\gamma', \gamma')_{Nk}\)

The positivity of \((\gamma', \gamma')_{Nk}\) is easily established in at least a number of cases of physical interest:

(i) \(k = 1\): \((\gamma', \gamma')_{N1}\) was shown earlier to be the incident probability current. Hence, \((\gamma', \gamma')_{N1}\) is positive.

(ii) \(k\) arbitrary: It has been shown elsewhere that \((\partial p_N/\partial \alpha_k)\lambda\) equals \(\sqrt{\gamma'} \int \sqrt{g} \prod_{\mu=1}^{N} d\tilde{q}_\mu / p_N f_N(\gamma', \gamma')_{Nk}\), where \(\lambda\) is the totality of quantum numbers characterizing \(\gamma'\). The numerator is positive since \(\sqrt{g} \prod_{\mu=1}^{N} d\tilde{q}_\mu\) is a volume element. \(p_N\) and (without loss of generality) \(f_N\) are also positive. When \(p_N\) is a monotonic function of \(\alpha_k\) at a given \(\lambda\), and so has a constant sign, one can then choose the sign of \(\alpha_k\) so that \((\partial p_N/\partial \alpha_k)\lambda\) is positive. In at least one typical choice of \(\alpha_k\) of physical interest described elsewhere, \(p_N\) depends only on one \(\alpha_k\) \((\partial p_N/\partial \alpha_k)\lambda\) then equals \(dp_N/d\alpha_k\) and, according to (36), equals \(\phi_{Nk}/p_N\).
References

1. P. Stäckel, Habilitationsschrift, Halle (1891). (I am indebted to the librarian of Princeton University for a photostat copy of this manuscript). In deriving the necessary conditions Stäckel considered a general coordinate system; in deriving the sufficient ones he considered orthogonal systems.

2. H. P. Robertson, Math. Ann. 98, 749 (1927). The similarity of conditions noted refers to those for the only coordinate systems considered by Robertson, namely orthogonal ones. Parenthetically, it may be noted that in some non-Euclidean spaces for which n>3, it is impossible to find a set of orthogonal coordinates (e.g. ref. 7b, pp. 45 and 104).


7. (a) More precisely, when the coordinates are orthogonal the quantities reciprocal to $g_{rs}$, $g_{rs}$, are diagonal. However, since $g_{rs}$ is the cofactor of $g_{rs}$, where $g$ is the $n \times n$ determinant of the $g_{rs}$, and since $g_{rs}$ is diagonal, so is $g_{rs}$.

(b) E. g., C. E. Weatherburn, Riemannian Geometry, Cambridge University Press (1957), Eq. 11, p. 41.

8. In this case, by suitable numbering of the coordinates, the nonvanishing elements in the $g_{rs}$ determinant occur in blocks along the diagonal, one block for each set of coordinates; $g_{rs}$ vanishes when $r$ and $s$ belong to different sets. It can then be shown that $g_{rs}$ also vanishes for such pairs of $r$ and $s$.

9. To obtain (II) one first computes a determinant from (II):

$$h_{\mu} \det g_{ij} = \phi_{\mu_i \lambda} h_{\mu} \det f^{\mu_i \mu_j}_{i,j=1}$$
10. E.g., Eq. 1.8 in Ref. 4 can be solved for a quantity $P_i$ knowing the metric tensor. With the aid of (2.1) there, one finds thereby $\phi^* \rho / \phi$, from which $\phi$ is immediately calculated: $\phi$ equals $\left[ \det(\phi^* \rho / \phi) \right]^{-1/2}$, $\rho_i$ is then obtained by inversion. However, a much more direct method of obtaining $\phi_i$ from the metric tensor can probably be found.

11. The expression for a "probability current density" in curvilinear coordinates is given in ref. 6, p. 40. It equals $I \sqrt{g}$, aside from a term of magnetic origin. No use was made of covariant and contravariant forms, and so the expression cited does not emphasize its invariant property. Nevertheless, it would lead to Eq. (24) when used to calculate $J$ for the current through a coordinate hypersurface.


14. If $\lambda$ is the unit normal to $S_N$, then one can show: $\sum_{j=1}^{n} \gamma_j = \delta_{1N} / \sqrt{g_{NN}}$, as follows: Let $\lambda$ be any vector which lies in $S_N$ but which is otherwise arbitrary. Since $S_N$ contains coordinate curves but that of $q^N$ (each of them is at the intersection of $S_N$ with any $n-2$ other coordinate hypersurfaces) we can chose $\lambda$ so that only the $i$th component $\lambda_i$ does not vanish ($i \neq N$). $\lambda \cdot \lambda$ equals $\sum_{j=1}^{n} \gamma_j \lambda_i$ i.e. $\gamma_i \lambda_i$. Since $\lambda$ is normal to $S_N$, $\lambda \cdot \lambda$ vanishes and therefore, so does $\gamma_i$ ($i \neq N$). Since $\lambda$ is a unit normal then $g_{NN} \gamma_{i} = 1$, i.e. $\gamma_{i} = \delta_{iN} / \sqrt{g_{NN}}$. $\gamma_{N}$ equals $\delta_{N} / \sqrt{g_{NN}}$.


16. I.e., a coordinate curve which extends to infinity. Under certain conditions (25) is also applicable over arcs of closed coordinate curves such as circles or ellipses.

17. We have applied the method given in Jeffreys and Jeffreys, Methods of Mathematical Physics, Cambridge University Press (1962), p. 522, by first introducing a change of dependent variable $Y_N = Y_N / \sqrt{T_N}$ and then obtaining the asymptotic solution for $Y_N$ under the typical conditions of $X_N$ real. (exp$(i \int X_N^{1/2} dN) / \sqrt{T_N} X_N^{1/4}$ then describes an infinitely long wave train). The $X$ here is $iX$ on p. 522.

19. Using (1) one sees that the factor multiplying the differential operator in the integrand is $-2 \frac{\mu \nu}{\kappa^2 \rho} \phi^{11} f_N$. Both $\mu \nu$ and $\phi^{11}$ are independent of the coordinates in set $\mu$, since both are minors in $\phi$ not involving the $\mu$'th row. Eq. (44) then follows upon integration by parts.


22. From Eq. (II) one finds that $\phi^{11} = 1$ and $\phi^{21} = \frac{1}{r^2 \sin \theta}$. Since $\phi^{11}$ and $\phi^{21}$ are the cofactors of $\phi^{11}$ and $\phi^{21}$ in the determinant $\phi$, they equal $\phi_{22}$ and $\phi_{12}$. One thus finds $\phi_{22}/\phi_{12} = \frac{1}{r^2 \sin \theta}$. Since $\phi_{22}$ is a function of $(r, \theta)$ and $\phi_{12}$ is a function only of $r$ we can set them equal to $\sin \theta$ and $r^{-2}$, respectively. Since $\phi^{11}$ equals $\phi_{22}$, we then find $\phi = \sin \theta$.

23. Ref. 7b, p. 42.