

Optimal Separation of Center-of-Mass Motion*

C. M. Vincent

Physics Department, University of Pittsburgh, Pittsburgh, Pennsylvania 15213

(Received 14 March 1973)

It is shown that a given approximate eigenfunction F of a many-body Hamiltonian can be improved by exploiting the separation of the exact eigenfunction in internal and c.m. coordinates. The method given leads reliably to a lower energy for the ground state, without requiring the solution of an additional dynamical problem. The best internal wave function (BIWF) is taken to be the internal factor of the separable wave function that has the largest possible overlap with F . The existence, uniqueness, and construction of the BIWF are derived. A canonical expansion $F = \sum a_i \Psi_i \psi_i$ is described, in which Ψ_i are *orthogonal* functions of the c.m. coordinates, and ψ_i are *orthogonal* functions of the internal coordinates. The canonical expansion is shown to converge faster than any other. It is applied to the discussion of the "projection" or "generator-coordinate" treatment of c.m. motion using arbitrary c.m. wave functions. It is shown that the Gartenhaus-Schwartz prescription is not equivalent to the use of any internal wave function, and gives systematically worse results for off-diagonal matrix elements than for expectation values.

1. INTRODUCTION

In the nonrelativistic quantum-mechanical treatment of an isolated system, the Hamiltonian can always be written in the form¹

$$H = H_{\text{int}} + (2M)^{-1}P^2, \quad (1)$$

where P and M are the total momentum and mass, respectively, and H_{int} acts only on internal variables. This separation is illustrated (quite adequately for the purposes of the present paper) by a system of two particles moving in one dimension. The coordinates, masses, and momenta of the particles are respectively denoted by x_i , m_i , and p_i for $i = 1, 2$. Then the c.m. coordinate R and total momentum P are defined by

$$R = \frac{m_1 x_1 + m_2 x_2}{M}, \quad P = P_1 + P_2.$$

In this particular example, the only internal coordinate is

$$r = x_1 - x_2,$$

and its conjugate momentum is

$$p = \mu \left(\frac{p_1}{m_1} - \frac{p_2}{m_2} \right),$$

in terms of the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Let $V(r)$ be the interaction between the particles. Then Eq. (1) is satisfied with

$$H_{\text{int}} = (2\mu)^{-1}p^2 + V(r).$$

It is easily seen that H_{int} commutes with both R and P . This is a formal way of saying that

H_{int} acts only on the internal coordinates. The validity of the following considerations is not restricted by the presence of only a single internal coordinate r in the example chosen for illustration.

Rotational invariance and other well-known symmetries are often valuable in simplifying the solution of the Schrödinger equation. In the same way, one would like to exploit the separation of H that Eq. (1) expresses. An *exact* eigenfunction F of the Hamiltonian H , which satisfies

$$HF = EF,$$

will always be of the form

$$F_{P'}(R, r) = e^{iP'R} \psi(r),$$

where P' is an eigenvalue of the total momentum. Here $\psi(r)$ will be called the internal wave function. It is natural² to look for an eigenfunction of H_{int} rather than of H . Exact eigenfunctions of H_{int} are always of the form

$$F_{\text{exact}}(R, r) = \Psi(R) \psi(r). \quad (2)$$

Because H_{int} does not act on R , any c.m. wave function $\Psi(R)$ is acceptable. Therefore, it is the *separability* in R and r that is essential to good c.m. behavior, rather than the particular form $e^{iP'R}$ for the c.m. wave function.

Many approximation schemes for the many-particle problem in quantum mechanics lead to wave functions that lack the property (2). An important example of such a scheme is the shell-model method, in which a translationally non-invariant single-particle potential is introduced. Several approaches to the resulting "c.m. problem" have been devised. In discussing these, it is necessary to clearly recognize that Eq. (2) is no

more essential than other fundamental properties of the exact eigenfunction. Every approximate eigenfunction of the Hamiltonian violates at least one fundamental requirement on the exact eigenstate (namely the factorizability of its time dependence). It is nevertheless possible to make meaningful calculations using such a wave function. Similarly, the separability property (2) need not be *required* of an approximate wave function. However (as will be shown) Eq. (2) can be used to *improve* a given approximate wave function.

Most treatments of the c.m. motion involve the construction of an internal wave function $\psi(r)$ from the given approximate wave function $F(R, r)$. Many such treatments belong to the class of "projection methods" or "generator-coordinate methods".³ In methods of this type, the internal wave function is taken to be

$$\psi(r) = N \int dR g(R) F(R, r), \quad (3)$$

where N is a normalization constant and $g(R)$ is a c.m. wave function. Various authors have chosen the c.m. wave function $g(R)$ in various ways.³ Popular choices have been $\delta(R)$, $e^{iP'R}$, and a harmonic-oscillator ground state.

It will be shown that projection methods with arbitrarily chosen $g(R)$ have little claim to special merit. Their use is not always disastrous, however, because if F satisfies Eq. (2) exactly, the choice of $g(R)$ does not affect the resulting internal state $\psi(r)$. For example, all projection methods will give the same results when applied to an anti-symmetric shell-model state constructed from a ground-state harmonic-oscillator configuration, because for this case the wave function is separable.⁴ If the separability of F is not exact, the choice of $g(R)$ does make some difference, but if F is nearly separable, the difference is likely to be small. The present work therefore concentrates on the nontrivial case where F is not separable.

Ernst, Shakin, and Thaler⁵ have described a projection method in which $g(R)$ is chosen to minimize the expectation $\langle \psi | H_{\text{int}} | \psi \rangle$. Not surprisingly, this choice of $g(R)$ leads to the $\psi(r)$ that has the largest possible overlap with the true ground state of H_{int} . However, by insisting too heavily on the separability requirement [Eq. (2)], this approach leads to an unnecessarily difficult procedure. Presumably, as much effort as possible has already been devoted to the calculation of $F(R, r)$. If it were technically feasible to minimize $\langle \psi | H_{\text{int}} | \psi \rangle$ with an internal wave function ψ of the same generality as F , this would more easily be done directly, without the intrusion of an unseparated wave function $F(R, r)$. After all, it is easy to construct a family of internal wave functions. What is not so easy is to diagonalize H_{int} in a space of in-

ternal wave functions, and in the method of Ernst, Shakin, and Thaler this task remains to be done. Given $F(R, r)$, the real need is for a reliable method of choosing $g(R)$ without further dynamical calculation. The present paper will describe such a method.

The rational choice of $g(R)$ always involves a difficult calculation. Indeed, the method to be described is perhaps more useful as a standard with which other nondynamical methods can be compared, than as a tool for practical calculations. In Sec. 2, the method is described, and in Sec. 3 it is applied to the discussion of projection methods. Section 4 contains a discussion and critique of the Gartenhaus-Schwartz prescription, which is shown not to correspond to the use of any internal wave function.

2. OPTIMAL SEPARATION OF INTERNAL AND c.m. VARIABLES

The proposed construction of the best separable approximation $\Psi(R)\psi(r)$ is most compactly described by introducing Hermitian c.m. and internal density operators D and d , defined by the kernels

$$\langle r | d | r' \rangle = \int dr F(R, r) F(R, r')^*, \quad (4a)$$

$$\langle R | D | R' \rangle = \int dr F(R, r) F(R', r)^*. \quad (4b)$$

It is assumed that F is a bound state, so that $\int dR \int dr |F|^2 = 1$. The following mathematical results are proved in Appendix I:

(a) The operators D and d have the same eigenvalues λ_i . The eigenvalues are all discrete, and satisfy

$$1 \geq \lambda_0 \geq \lambda_1 \geq \lambda_2 \geq \dots \geq 0.$$

The only possible point of condensation of eigenvalues is $\lambda = 0$. The corresponding eigenfunctions Ψ_i and ψ_i can be taken as orthonormal sets, satisfying

$$D\Psi_i = \lambda_i \Psi_i, \quad d\psi_i = \lambda_i \psi_i,$$

and

$$\langle \Psi_i | \Psi_j \rangle = \langle \psi_i | \psi_j \rangle = \delta_{ij}.$$

(b) Of all possible normalized separable wave functions $\Psi(R)\psi(r)$, the one that has the greatest possible overlap with $F(R, r)$ [i.e., the maximum value of $\int dR \int dr F(R, r) \Psi(R) \psi(r)$] is obtained by choosing $\Psi(R) = \Psi_0$ and $\psi(r) = \psi_0$. That is, the optimal c.m. and internal wave functions are, respectively, the eigenfunctions of D and d that belong to the largest eigenvalue.

(c) F can be expanded in the form

$$F(R, r) = \sum_{i=0}^{\infty} a_i \Psi_i(R) \psi_i(r), \quad (5)$$

where Ψ_i and ψ_i are normalized eigenfunctions of D and d , respectively, and $|a_i|^2 = \lambda_i$. (Note that both the Ψ_i and the ψ_i are orthogonal sets.)

(d) Of all possible N -term sums of the form

$$F_N = \sum_{i=0}^{N-1} b_i \Phi_i(R) \phi_i(r)$$

(with ϕ_i an orthonormal set and Φ_i arbitrary), the one that minimizes $\int dR \int dr |F_N - F|^2$ is

$$F_N = \sum_{i=0}^{N-1} a_i \Psi_i \psi_i,$$

that is, the first N terms of (5).

It is convenient to refer to Eq. (5) as the "canonical expansion of F ". Result (d) shows that the canonical expansion of F converges more rapidly than any other.

The central result of the present work is that $\psi_0(r)$ is the best possible internal wave function that can be derived from $F(R, r)$ by purely kinematic means. By multiplying Eq. (5) by $\Psi_0(R)^*$ and integrating with respect to R , it follows that

$$\psi_0(r) = a_0 \int dR \Psi_0(R)^* F(R, r). \quad (6)$$

Therefore ψ_0 , the best internal wave function (BIWF), is obtained by applying the projection method (3) to F with $g(R) = \Psi_0(R)$.

The BIWF will be a better approximation to an exact eigenstate of H_{int} than is the nonseparable wave function F , provided that F is already very nearly an eigenstate of H_{int} . A more precise statement applies when F is an approximation to $\psi_{\text{g.s.}}$, the ground-state wave function, which belongs to the eigenvalue $E_{\text{g.s.}}$ of H_{int} . Suppose that the ψ_0 derived from F is a good approximation to $\psi_{\text{g.s.}}$, so that

$$\int dr \psi_0^* H_{\text{int}} \psi_0 = E_{\text{g.s.}} + \Delta, \quad (7a)$$

where Δ is small. Then it follows that

$$\left| \int dr \psi_{\text{g.s.}}^* \psi_0 \right|^2 = 1 - \epsilon, \quad (7b)$$

where ϵ is small and positive. In Appendix II conditions (7) are shown to imply that

$$\int dR \int dr F^* H_{\text{int}} F - \int dr \psi_0^* H_{\text{int}} \psi_0 > \eta > 0, \quad (8)$$

where

$$\eta \approx (1 - |a_0|^2)(E_1 - E_{\text{g.s.}}),$$

provided that $\epsilon \ll 1$ and $\Delta \ll E_1 - E_{\text{g.s.}}$, E_1 being the energy of the first excited state. It follows that if F is a sufficiently good approximation to $\psi_{\text{g.s.}}$, the BIWF ψ_0 leads to a lower expectation value of H_{int} than is obtained from the original nonseparable wave function F . If $|a_0|^2$ is not close to unity, the lowering of the ground-state energy may be considerable.

In summary, the BIWF ψ_0 [which results by projecting with the optimal choice of $g(R)$, namely $\Psi_0(R)$] will always be an improvement on the nonseparable state F , provided that F is very nearly an eigenfunction of H_{int} . It is rather remarkable that one can gain an improvement without expending further effort on dynamical calculations. However, the calculation of ψ_0 is quite laborious. First, D must be constructed. This will involve integration over all internal coordinates, which is difficult, though easier than the construction of the matrix of H_{int} in internal states. Next, the largest eigenvalue λ_0 of D and its corresponding eigenfunction Ψ_0 must be found. Because D is a Hilbert-Schmidt operator,⁶ it can be arbitrarily well represented by a finite matrix. Therefore there is no theoretical obstacle to this step, and it is appreciably easier than the diagonalization of a many-body internal Hamiltonian. The evaluation of ψ_0 from Eq. (6) is comparatively easy.

Our choice of $\psi(r) = \psi_0(r)$ differs from the internal wave function constructed by Ernst, Shakin, and Thaler.⁵ The function $F(R, r)$ can be regarded as a family of functions of r , labeled by a parameter R . The internal wave function of Ernst, Shakin, and Thaler is an eigenfunction of H_{int} in the subspace of Hilbert space that is spanned by the family $F(R, r)$. Our internal wave function $\psi_0(r)$ lies in the same subspace, but is not necessarily an eigenfunction of H_{int} in this subspace. Therefore, $\psi_0(r)$ will not give as low a ground-state energy as the Ernst, Shakin, and Thaler wave function. However, $\psi_0(r)$ is much easier to calculate, and also guarantees a lower ground-state energy than $F(R, r)$.

3. COMPARISON OF ARBITRARY AND OPTIMAL PROJECTION METHODS

The chief use of wave functions is to calculate matrix elements of physically interesting operators. The canonical expansion of $F(R, r)$ will now be used to discuss matrix elements of operators between wave functions obtained by projection methods of the type (3) using arbitrary c.m. wave functions $g(R)$. The BIWF ψ_0 will be taken as a standard of comparison. Any operator A can be expanded as a sum of products of operators that act only on the internal coordinates with operators that act only on the c.m. By the separation property (2), it follows that the matrix elements of any operator between eigenstates of H_{int} can be expressed in terms of matrix elements (between c.m. wave functions) of operators that act only on the c.m., and matrix elements (between internal wave functions) of operators that act only on the internal coordinates. Because the c.m. motion

can be specified at will, matrix elements of operators that act only on internal coordinates are of prime interest. Let A_{int} be such an internal operator. Supposing F to be nearly separable, $F - \Psi_0 \psi_0$ can be regarded as a small quantity of first order. The arbitrary-projection method leads to an internal wave function that may be expanded in terms of the canonical internal states ψ_i as follows

$$\psi(r) = \sum_{i=0}^{\infty} a_i \langle g | \Psi_i \rangle \psi_i(r).$$

For the expectation of A_{int} , this gives

$$\langle \psi | A_{\text{int}} | \psi \rangle = \sum_{ij} a_i \langle g | \Psi_i \rangle a_j^* \langle \Psi_j | g \rangle \langle \psi_i | A_{\text{int}} | \psi_j \rangle.$$

In this expression there are cross terms between the large component $\psi_0(r)$ and the first-order small terms ψ_i ($i \neq 0$). Therefore the deviation from the BIWF result is of first order. There is therefore no reason to believe that the projection method with arbitrary $g(R)$ gives any improvement. In fact, for the cross terms to be absent, it is necessary for g to be orthogonal to all Ψ_i that belong to nonvanishing eigenvalues of D (except Ψ_0). An example of the failure of arbitrary projection methods is mentioned by Ernst, Shakin, and Thaler.⁵ They remark that the use of an arbitrary $g(R)$ does not necessarily lower the ground-state energy. The case of off-diagonal elements is similar to that of diagonal elements, and nothing new emerges from it.

4. CRITIQUE OF THE GARTENHAUS-SCHWARTZ PRESCRIPTION

In calculating matrix elements of internal operators between internal wave functions, explicit construction of the internal wave functions can apparently be avoided by a method due to Gartenhaus and Schwartz (GS).⁷ For two nonseparable approximate eigenfunctions of H_{int} denoted by F_1 and F_2 , GS point out that the functions defined by

$$\psi_{\alpha}^{\text{GS}} = \lim_{\Lambda \rightarrow \infty} U_{\Lambda} F_{\alpha} \quad (\alpha = 1, 2)$$

depend on r only, where the unitary operator U_{Λ} depends on the parameter Λ as follows:

$$U_{\Lambda} = e^{i\Lambda(RP+PR)}.$$

For any internal operator A_{int} , GS derive the formal result

$$\langle \psi_{\alpha}^{\text{GS}} | A_{\text{int}} | \psi_{\beta}^{\text{GS}} \rangle = \lim_{\Lambda \rightarrow \infty} \langle F_{\alpha} | U_{\Lambda}^{-1} A_{\text{int}} U_{\Lambda} | F_{\beta} \rangle \quad (\alpha, \beta = 1, 2). \quad (9)$$

The method is appealing, because

$$\lim_{\Lambda \rightarrow \infty} U_{\Lambda}^{-1} A_{\text{int}} U_{\Lambda}$$

is easy to evaluate. In fact, since A_{int} commutes with R and P ,

$$\lim_{\Lambda \rightarrow \infty} U_{\Lambda}^{-1} A_{\text{int}} U_{\Lambda} = A_{\text{int}}.$$

Equation (9) then gives

$$\langle \psi_{\alpha}^{\text{GS}} | A_{\text{int}} | \psi_{\beta}^{\text{GS}} \rangle = \langle F_{\alpha} | A_{\text{int}} | F_{\beta} \rangle \quad (\alpha, \beta = 1, 2). \quad (10)$$

We now show that Eq. (10) cannot be correct as written, because there exist no internal wave functions that will make the left-hand side equal to the right-hand side for all possible internal operators A_{int} . Taking the particular case of a diagonal matrix element ($\alpha = \beta$), and making a canonical expansion of F_{α} , we can write

$$\langle F_{\alpha} | A_{\text{int}} | F_{\alpha} \rangle = \sum_{i=0}^{\infty} |a_i|^2 \langle \psi_{\alpha i} | A_{\text{int}} | \psi_{\alpha i} \rangle. \quad (11)$$

Equation (11) is not the expectation of A_{int} in any pure internal state (or wave function) but is instead a weighted average of expectations in many different internal wave functions. In other words, the state of *internal* motion represented by F_{α} is not representable by a wave function; instead, it must be represented by a *statistical ensemble* of internal wave functions.

It is easy to show that

$$\langle F_{\alpha} | A_{\text{int}} | F_{\alpha} \rangle = \text{tr}(A_{\text{int}} d_{\alpha}),$$

where d_{α} is the internal density matrix defined by Eq. (4a). This density matrix represents a state describable by a wave function $\psi(r)$ (pure state) if and only if it is of the form

$$\langle r | d_{\alpha} | r' \rangle = \psi(r) \psi(r')^*. \quad (12)$$

It follows from Eq. (12) that

$$\text{tr}(d_{\alpha}^2) = (\text{tr} d_{\alpha})^2. \quad (13)$$

Is it possible that the internal density matrix sometimes corresponds to an internal wave function? Appendix III shows that Eq. (13) (the condition for d_{α} to be representable by a wave function) is satisfied if and only if $F_{\alpha}(R, r)$ is separable. Hence, except in the trivial case of separable F_{α} , d_{α} does not correspond to any internal wave function. This establishes our conclusion that it is impossible to find internal wave functions $\psi_{\alpha}^{\text{GS}}$ and ψ_{β}^{GS} such that Eq. (10) holds for all possible A_{int} .

The nonexistence of $\psi_{\alpha}^{\text{GS}}$ and ψ_{β}^{GS} that satisfy Eq. (10) should not be surprising. Singular limiting operations often lead to such paradoxes. (For example, the *unitary* operator $e^{i\Lambda R}$ tends to zero in the limit $\Lambda \rightarrow \infty$, in the sense that its matrix elements between any square-integrable functions tend to zero.) Previous authors do not seem to have been aware of this defect of the GS method. However, Palumbo⁸ has commented that the GS

matrix elements [Eq. (10)] are equal to those that result from direct use of the uncorrected wave functions F_α and F_β . From this, he concludes that the GS method cannot satisfactorily correct for c.m. motion. Furthermore, Ernst, Shakin, and Thaler⁹ have shown that Eq. (9) gives a different result if U_Λ and U_Λ^{-1} are replaced by U_{Λ_1} and $U_{\Lambda_2}^{-1}$, where Λ_1 and Λ_2 tend to infinity independently.

Although the GS method does not correspond to the use of internal wave functions, it is not completely invalid. To compare the GS result with the BIWF result for expectation values, we write

$$\langle F_\alpha | A_{\text{int}} | F_\alpha \rangle = \langle \psi_{\alpha 0} | A_{\text{int}} | \psi_{\alpha 0} \rangle + \sum_{i=1}^{\infty} |a_i|^2 \times (\langle \psi_{\alpha i} | A_{\text{int}} | \psi_{\alpha i} \rangle - \langle \psi_{\alpha 0} | A_{\text{int}} | \psi_{\alpha 0} \rangle).$$

The first term is the BIWF result. If we regard a_i ($i \neq 0$) as small quantities of first order, we see that the GS result differs from the BIWF only by terms of second order. In this sense, the GS prescription gives *better* results for diagonal matrix elements than projection methods with arbitrary choice of $g(R)$.

Next consider off-diagonal matrix elements. In this case, F_1 and F_2 must each be expanded in terms of eigenfunctions of the corresponding density operators d_1, D_1 and d_2, D_2 . These expansions can be written

$$F_\alpha = \sum_i a_{\alpha i} \psi_{\alpha i}(R) \psi_{\alpha i}(r) \quad (\alpha = 1, 2).$$

Because Ψ_{1j} and Ψ_{2j} are eigenfunctions of different operators, the functions with $i \neq j$ need not be orthogonal. In the expansion

$$\langle F_1 | A_{\text{int}} | F_2 \rangle = \sum_{ij} a_{1j}^* a_{2j} \langle \Psi_{1j} | \Psi_{2j} \rangle \langle \psi_{1i} | A_{\text{int}} | \psi_{2j} \rangle,$$

the cross terms between large and small components of the wave function survive. Therefore, the GS result for an off-diagonal matrix element

differs from the BIWF result by terms of *first* order in a_{1i} ($i \neq 0$) and a_{2j} ($j \neq 0$). Thus we conclude that the GS result is systematically less reliable for off-diagonal elements than for expectation values.

5. DISCUSSION AND CONCLUSIONS

Surprisingly, it has been shown that a given nonseparable approximate eigenfunction of H_{int} can be improved without further reference to H_{int} , by exploiting the separation property of the exact eigenfunction. To be sure of an improvement, one must project with the optimal c.m. wave function $\Psi_o(R)$. If the calculation of $\Psi_o(R)$ is impracticable, one may calculate approximate matrix elements of observables without correcting the wave functions for c.m. motion. Then, as always, it is appropriate to use internal operators. The resulting procedure is exactly the GS prescription for calculating matrix elements. For diagonal elements, this turns out to be preferable to correcting for c.m. motion by a projection that uses an arbitrary c.m. wave function. It is therefore better to disregard the c.m. "problem" than to treat it arbitrarily.

It may be possible to extend the present analysis to other forms of collective motion—in particular, rotations of atomic nuclei. The separation property (2) will no longer be exact, and the rotational coordinates (analogous to R) will no longer be uniquely defined. However, there is hope of using the present theory to define a best intrinsic state [analogous to $\psi(r)$].

ACKNOWLEDGMENT

This paper owes its existence to the relentless encouragement and kind criticism of Norman Austern.

APPENDIX I: DERIVATION OF RESULTS (a)-(d)

(a) If ψ_i is an eigenfunction of d belonging to the eigenvalue λ_i , then the function

$$\Phi(R) = \int dr \psi_i(r) F(R, r)$$

is an eigenfunction of D (belonging to eigenvalue λ_i), because

$$\begin{aligned} D\Phi(R) &= \int dR' (R|D|R') \Phi(R') \\ &= \int dR' \int dr' F(R, r') F(R', r')^* \int dr \psi_i(r) F(R', r) \\ &= \int dr' F(R, r') \int dr \int dR' F(R', r) F(R', r')^* \psi_i(r) \\ &= \int dr' F(R, r') \int dr \langle r|d|r' \rangle \psi_i(r) = \int dr' F(R, r') [d\psi_i(r')]^* \\ &= \int dr' F(R, r') \lambda_i \psi_i(r')^*. \end{aligned}$$

Hence $\Phi(R) = \lambda_i \Phi_i(R)$ is proportional to $\Psi_i(R)$, the i th normalized eigenfunction of D . Similarly, every eigenvalue of D is an eigenvalue of d . D is a Hilbert-Schmidt operator by Schwarz's inequality, because

$$\begin{aligned} \text{tr}(D^2) &= \int dR \int dR' \left| \int dR F(R, r) F(R', r)^* \right|^2 \\ &< \int dR \int dr |F(R, r)|^2 \int dR' \int dr' |F(R', r')|^2 = 1. \end{aligned}$$

Therefore the eigenvalues λ_i are all discrete, and zero is their only possible limit point.⁷ The fact that $\text{tr} D = \sum_0^\infty \lambda_n = 1$ implies that $\lambda_n \rightarrow 0$ faster than n^{-1} .

(b) The overlap

$$a = \int dr \int dR F(R, r)^* \Psi(R) \psi(r)$$

can be written as a matrix element

$$a = \langle \Psi | \Omega | \psi \rangle \equiv \int dR \int dr \Psi(R) \langle R | \Omega | r \rangle \psi(r) \quad (14)$$

of an operator Ω which maps internal wave functions into c.m. wave functions. Ω must have the kernel

$$\langle R | \Omega | r \rangle = F(R, r)^*.$$

By direct calculation,

$$\Omega^\dagger \Omega = d. \quad (15)$$

If we define an orthogonal projection Q by

$$Q^2 = Q = Q^\dagger, \quad Q\Psi(R)^* = 0,$$

we can use Eqs. (14) and (15) to obtain

$$|a|^2 = \langle \psi | d | \psi \rangle - \langle \psi | \Omega^\dagger Q \Omega | \psi \rangle. \quad (16)$$

Both terms on the right of Eq. (16) are nonnegative. Therefore $|a|^2$ will be greatest when the first term is maximized and the second term is minimized. For normalized ψ , the first term is maximized by taking $\psi = \psi_0$ (the eigenfunction of d belonging to its largest eigenvalue). Fortunately, the second term can *simultaneously* be reduced to zero by choosing $\Psi = N(\Omega\psi)^*$, which is normalized if $|N|^2 = |\langle \psi | \Omega^\dagger \Omega | \psi \rangle|^{-1}$. This gives

$$\Psi = N(\Omega\psi)^* = N \int dr F(R, r) \psi^* = \Psi_0.$$

The maximum possible value of $|a|^2$ is simply the maximum possible value of $\langle \psi | d | \psi \rangle$, which is λ_0 , the largest eigenvalue of d (or D).

(c) $F(R, r)$ may be expanded in terms of $\psi_i(r)$, any complete orthonormal set of functions of r , as follows

$$F(R, r) = \sum_{i=1}^{\infty} F_i(R) \psi_i(r). \quad (17)$$

In general, the coefficient functions

$$F_i(R) = \int dr F(R, r) \psi_i(r)^*$$

are not orthogonal functions of R . However, when the ψ_i are chosen to be orthogonal eigenfunctions of d ,

the scalar product of F_i and F_j is

$$\begin{aligned} \int dR F_i(R)^* F_j(R) &= \int dR \int dr \int dr' F(R, r)^* \psi_i(r) F(R, r') \psi_j^*(r') \\ &= \int dr \int dr' \psi_j^*(r') (r' | d | r) \psi_i(r) \\ &= \lambda_i \int dr \psi_j^*(r) \psi_i(r) = \lambda_i \delta_{ij}. \end{aligned} \quad (18)$$

It follows that different $F_i(R)$ are orthogonal. By result (a), F_i is proportional to the normalized eigenfunction Ψ_i of D . That is, there exist normalization constants a_i such that

$$F_i = a_i \Psi_i. \quad (19)$$

From Eq. (18), it follows that

$$|a_i|^2 = \lambda_i.$$

The canonical expansion (5) results when Eq. (19) is substituted into Eq. (17).

(d) The proof given is an adaptation of the proof by Smith of a similar theorem relating to reduced density matrices.¹⁰

In Dirac notation for scalar products, the quantity to be minimized is

$$\langle F - F_N | F - F_N \rangle = 1 - 2\text{Re}\langle F | F_N \rangle + \langle F_N | F_N \rangle. \quad (20)$$

Define the nonnegative quantity

$$\delta \equiv \sum_{i=0}^{N-1} \int dR \left| \Phi_i(r) - \int dr F(R, r) \phi_i(r)^* \right|^2.$$

It can be shown directly that

$$\delta = \langle F_N | F_N \rangle - 2 \text{Re} \langle F | F_N \rangle + \sum_{i=0}^{N-1} \langle \phi_i | d | \phi_i \rangle. \quad (21)$$

By combining Eqs. (20) and (21), it follows that

$$\langle F - F_N | F - F_N \rangle = 1 - \sum_{i=0}^{N-1} \langle \phi_i | d | \phi_i \rangle + \delta. \quad (22)$$

This quantity is minimized by maximizing the second term, and minimizing δ . The second term is an absolute maximum (for all possible *orthonormal* sets ϕ_i) when $\phi_i = \psi_i$, the N eigenfunctions of d belonging to its N largest eigenvalues. With this choice of ϕ_i , one can make δ an absolute minimum (in fact, zero). The correct choice is clearly

$$\Phi_i(R) = \int dr F(R, r) \psi_i(r)^* = F_i(R).$$

By Eq. (19), this is

$$\Phi_i(R) = a_i \Psi_i(R).$$

It follows that $\langle F - F_N | F - F_N \rangle$ is a minimum when F_N is the first N terms of the canonical expansion (5).

APPENDIX II: PROOF THAT THE BIWF LOWERS THE GROUND-STATE ENERGY

Let Π be the orthogonal projection on $\psi_{g.s.}$, the internal wave function of the ground state. In Dirac notation, Eq. (7a) becomes

$$\langle \psi_0 | H_{int} | \psi_0 \rangle = E_{g.s.} + \Delta,$$

and Eq. (7b) becomes

$$\langle \psi_0 | \Pi | \psi_0 \rangle = 1 - \epsilon.$$

For the expectation values with $i \neq 0$ we have

$$\begin{aligned} \langle \psi_i | H_{int} | \psi_i \rangle &= \langle \psi_i | \Pi H \Pi | \psi_i \rangle + \langle \psi_i | (1 - \Pi) H_{int} (1 - \Pi) | \psi_i \rangle \\ &> E_{g.s.} \langle \psi_i | \Pi | \psi_i \rangle + E_1 \langle \psi_i | (1 - \Pi) | \psi_i \rangle, \end{aligned} \quad (23)$$

because $\Pi \psi_i$ belongs to the eigenvalue $E_{g.s.}$ and $(1 - \Pi) \psi_i$ is a linear combination of eigenfunctions of H_{int} that belong to E_1 and higher eigenvalues. Now because $\psi_{g.s.}$ is normalized,

$$\text{tr} \Pi = \text{tr} (| \psi_{g.s.} \rangle \langle \psi_{g.s.} |) = 1 = \langle \psi_0 | \Pi | \psi_0 \rangle + \sum_{i \neq 0} \langle \psi_i | \Pi | \psi_i \rangle.$$

By applying Eq. (7b), it then follows that

$$\langle \psi_i | \Pi | \psi_i \rangle < \epsilon \quad (i \neq 0). \quad (24)$$

By applying Eqs. (24) and (7a) to the inequality (23), it can be shown that

$$\langle \psi_i | H_{\text{int}} | \psi_i \rangle - \langle \psi_0 | H_{\text{int}} | \psi_0 \rangle > (E_1 - E_{g.s.})(1 - \epsilon) - \Delta. \quad (25)$$

Finally, Eq. (25) can be applied to the canonical expansion (5) to show that

$$\begin{aligned} \langle F | H_{\text{int}} | F \rangle - \langle \psi_0 | H_{\text{int}} | \psi_0 \rangle &= \sum_{i=1}^{\infty} |a_i|^2 (\langle \psi_i | H_{\text{int}} | \psi_i \rangle - \langle \psi_0 | H_{\text{int}} | \psi_0 \rangle) \\ &> \sum_{i=1}^{\infty} |a_i|^2 [(E_1 - E_{g.s.})(1 - \epsilon) - \Delta] \\ &= (1 - |a_0|^2) [(E_1 - E_{g.s.})(1 - \epsilon) - \Delta]. \end{aligned}$$

If ϵ and Δ are neglected, this reduces to Eq. (8).

APPENDIX III: PURITY OF d AND SEPARABILITY OF F

Suppose d represents a pure internal state, so that

$$\text{tr}(d^2) - (\text{tr}d)^2 = \int d\mathbf{r} \int d\mathbf{r}' (|\langle \mathbf{r} | d | \mathbf{r}' \rangle|^2 - \langle \mathbf{r} | d | \mathbf{r} \rangle \langle \mathbf{r}' | d | \mathbf{r}' \rangle) = 0. \quad (26)$$

In terms of $F(R, r)$, the integrand is

$$I = \left| \int dR F(R, r) F(R, r') \right|^2 - \left[\int dR F(R, r) F(R, r) \right] \left[\int dR' F(R', r) F(R', r) \right]. \quad (27)$$

If $F(R, r)$ and $F(R, r')$ are regarded as two functions of R (depending on parameters r and r'), Schwarz's inequality¹¹ states that

$$I \leq 0. \quad (28)$$

Therefore Eq. (26) can be satisfied only if $I = 0$ for all r and r' . However, the equality in Eq. (28) holds only if $F(R, r)$ and $F(R, r')$ are proportional (considered as functions of R). That is, choosing some fixed value of r' ,

$$F(R, r) = G(r)F(R, r').$$

In other words, $F(R, r)$ must be separable in R and r .

The result can be generalized to apply to a *transition* density matrix of the type

$$\langle \mathbf{r} | d_{12} | \mathbf{r}' \rangle = \int dR F_1(R, r) F_2(R, r')^*,$$

and density matrices

$$\langle \mathbf{r} | d_{\alpha\alpha} | \mathbf{r}' \rangle = \int dR F_\alpha(R, r) F_\alpha(R, r')^* \quad (\alpha = 1, 2).$$

The condition for d_{12} to correspond to two pure internal states is

$$\text{tr}(d_{12} d_{12}^\dagger) - (\text{tr}d_{11})(\text{tr}d_{22}) = 0.$$

Schwarz's inequality can be used to show that this implies that both $F_1(R, r)$ and $F_2(R, r)$ are separable in R and r .

*Work supported in part by the National Science Foundation.

¹A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1965), pp. 365-366.

²K. T. R. Davies and R. L. Becker, *Nucl. Phys.* **A176**, 1 (1971); H. J. Lipkin, A. de Shalit, and I. Talmi, *Nuovo*

Cimento **2**, 773 (1955).

³H. J. Lipkin, *Phys. Rev.* **110**, 1395 (1958); R. E. Peierls and J. Yoccoz, *Proc. Phys. Soc. Lond.* **A70**, 381 (1957); and J. J. Griffin and J. A. Wheeler, *Phys. Rev.* **108**, 311 (1957).

⁴H. A. Bethe and M. E. Rose, *Phys. Rev.* **51**, 283 (1937);

- J. P. Elliot and T. H. R. Skyrme, Proc. R. Soc. A232, 561 (1955).
- ⁵D. J. Ernst, C. M. Shakin, and R. M. Thaler, Phys. Rev. C 7, 925 (1973).
- ⁶R. G. Newton, *Scattering Theory of Waves and Particles* (McGraw-Hill, New York, 1966), pp. 201-202.
- ⁷S. Gärtenhaus and C. Schwartz, Phys. Rev. 108, 482 (1957).
- ⁸F. Palumbo, Phys. Lett. 37B, 341 (1971).
- ⁹D. J. Ernst, C. M. Shakin, and R. M. Thaler, Phys. Rev. C 7, 1340 (1973).
- ¹⁰D. W. Smith, in *Reduced Density Matrices with Applications to Physical and Chemical Systems*, edited by A. J. Coleman and R. M. Erdahl (Queen's University, Kingston, Ontario, 1968); see also T. Ando, Rev. Mod. Phys. 35, 690 (1963); and P.-O. Löwdin and H. Shull, Phys. Rev. 101, 1730 (1956).
- ¹¹A. Messiah, see Ref. 1, p. 165.