PHYSICAL REVIEW VOLUME 187, NUMBER 1 5 NOVEMBER 1969

Variation-Iteration Method for Many-Particle Bound States*

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(Received 10 March 1969)

The extension to bound-state problems of the variational bound formulation of scattering theory is considered. The simple decaying boundary condition allows a wider class of projection operators than in scattering theory, and they can be used to arrange an accurate wave-function calculation. The method retains the extremum property of the Ritz principle.

I. INTRODUCTION

In connection with the variational bound formulation[1] of the low-energy scattering problems, a simple variation-iteration procedure was studied[2] previously. It treats the low-energy scattering problem in two steps; the virtual excitation effect due to the presence of closed channels is taken into account variationally, and enters as an inhomogeneous term of the open-channel scattering equation, which is then solved exactly numerically. The particular separation of the problem into two parts is necessary there to ensure the extremum property of the calculated scattering parameters. The iteration procedure makes it possible to avoid the explicit use of the "static" Green's function which would otherwise appear in the purely variational bound approach[1] and which would complicate the application.

We consider in this paper an extension of the above formalism to bound-state problems, and show that the method can be used with greater flexibility than in the scattering problems to obtain an improved variational wave function of high accuracy. The iteration procedure of Ref. 2 is especially useful here, since the bound-state energy is not known *a priori*, and consequently the static Green's function required in the noniterative procedure has to be evaluated repeatedly as the trial function and energy improve.

If the dominant component of the wave function of a bound state can be projected onto a subspace (the P space) and the equation for it solved exactly, while the more complicated but presumably smaller correction part (the Q space) is estimated variationally, then the sum of these two parts should result in an improved variational wave function. Effectiveness of such a procedure depends largely on the choice of the operators P and Q, and this can be done much more readily for the bound-state problem than for the scattering problem where the form of asymptotic channel functions has to be specified exactly.

II. FORMALISM

We consider an N-electron atom with an infinitely heavy nucleus and neglect the spin degrees of freedom, but we assume that the electrons obey the exclusion principle. The Hamiltonian is given by

$$H = \sum_{i=1}^{N} h(i) + \sum_{i>j}^{N} v(i,j), \qquad (2.1)$$

where $h(i) = t(i) + v(i)$,

$$t(i) = -\frac{\hbar^2}{2m}\nabla_{\vec{r}_i}^{\,2},$$

$$v(i) = -Ze^2/r_i, \quad v(i,j) = e^2/|\vec{r}_i - \vec{r}_j|,$$

and where the charge Z of the nucleus may not be equal to the number N of the electrons. The ith electron coordinates $\vec{r}_i$ is measured from the nucleus and is written simply as i for the argument of a function or an operator.

A. Projection Operators

We divide the bound-state wave function Ψ into two orthogonal components, using the projection operators P and Q which satisfy the usual properties:

$$P + Q = 1, \quad PQ = QP = 0,$$
$$P^2 = P = P^\dagger, \quad Q = Q = Q^\dagger. \qquad (2.2)$$

We then obtain the Feshbach equations[3]

$$P(H - E_0)\mathrm{P}\Psi = -PHQ\Psi, \qquad (2.3a)$$

$$Q(H - E_0)Q\Psi = -QHP\Psi, \qquad (2.3b)$$

where E_0 is the binding energy to be evaluated. The discussion will be restricted to the lowest state of the system with given symmetry and total spin and angular momenta, so that the extremum property of the resulting energy E_{0t} can be maintained readily. (For the excited states, the method described below may still be valid if the variational procedure for the calculation of $Q\Psi$ should be modified and if $P\Psi$ contains all the components of wave functions of the lower states such that the Hylleraas-Undheim theorem[4] is satisfied.) In (2.3), the form of P and Q is still arbitrary, and it is the main purpose of this paper to discuss various possible choices. If we write the effective single-particle operator $h^M(i)$ as

$$h^M(i) = t(i) + v^M(i), \tag{2.4}$$

where the model potential $v^M(i)$ may not necessarily be the same as $v(i)$ of (2.1), and construct a complete orthonormal set $\{\psi_n(i)\}$ from

$$h^M(i)\,\psi_n(i) = e_n\psi_n(i), \tag{2.5}$$

then the single-particle projection operators can be defined by

$$\begin{aligned} P_n(i;i') &= \psi_n(i))(\psi_n(i') \equiv P_n(i), \\ Q_n(i;i') &= \delta(i-i') - P_n(i;i') \equiv Q_n(i), \end{aligned} \tag{2.6}$$

with $P_n(i)^2 = P_n(i) = P_n(i)^\dagger$,

$$P_n(i)Q_n(i) = 0,$$

$$P_n(i)P_m(i) = \delta_{nm}P_n(i).$$

For an infinitely heavy nucleus assumed here, we have the important additional property that

$$[P_m(i),\ P_n(j)] = 0 \tag{2.7}$$

for all pairs of m,n and i,j.

In principle, we can also construct other more complicated many-particle operators from some model Hamiltonians which may contain interelectron interactions. However, it is in general difficult to construct such operators, and the simplest possible choice would certainly be the form which is a symmetric sum of products of the single-particle operators $P_n(i)$. We restrict our discussion to this simple case only, although the formalism presented here can be readily modified for other cases.

As a first choice within the above simplifying restriction, we consider operators of the form

$$\begin{aligned} P_\alpha{}^{\mathrm{HF}} &= \sum{}' P_{\alpha_1}(i)\cdots P_{\alpha_{N-1}}(j)P_{\alpha_N}(k), \\ Q_\alpha{}^{\mathrm{HF}} &= \prod_{i=1}^{N} \delta(i-i') - P_\alpha{}^{\mathrm{HF}}, \end{aligned} \tag{2.8}$$

where α denotes a set of N states, $\{\alpha_1, \cdots, \alpha_{N-1}, \alpha_N\}$, all of which are different from each other, and $\sum'$ denotes the sum of terms obtained by all possible permutations of N particle labels such that each particle label appears only once in each term. The resulting wave function assumes the usual form of the Hartree-basis function

$$\begin{aligned} P_\alpha{}^{\mathrm{HF}}\Psi = (N!)^{-1/2}\det[&\psi_{\alpha_1}(1)\cdots\psi_{\alpha_{N-1}}(N-1) \\ &\times\psi_{\alpha_N}(N)], \end{aligned} \tag{2.9}$$

and similarly for $Q_\alpha{}^{\mathrm{HF}}\Psi$. The best possible choice of $h^M(i)$ for the form (2.9) is well known to be the Hartree-Fock solution, with the self-consistent potential $v^{\mathrm{HF}}(i)$ given in a nonlocal form,

$$v^{\mathrm{HF}}(i) \equiv v^{\mathrm{HF}}(i;i') = (P_\alpha{}^{\mathrm{HF}}[H-H^M]\,P_\alpha{}^{\mathrm{HF}})_{-i}, \tag{2.10}$$

where $(\cdots)_{-i}$ indicates the integrations over all the variables involved except the ith and i'th, and we denote simply i for the set i and i', and where

$$H^M = \sum_{i=1}^{N}[t(i) + v^{\mathrm{HF}}(i)].$$

Obviously, one can improve the procedure by adding other states $P_{\alpha'}{}^{\mathrm{HF}}$. Since the approach with the choice (2.8) is well known, we do not pursue it further.

The second choice of P and Q we should like to explore is given by

$$\begin{aligned} P_\alpha = {} & \sum{}' P_{\alpha_1}(i)\cdots P_{\alpha_{N-1}}(j) \\ & -\frac{1}{2}\sum_{n=\alpha_1}^{\alpha_{N-1}}\sum{}' P_{\alpha_1}(i)\cdots P_{\alpha_{N-1}}(j)\,P_n(k), \end{aligned} \tag{2.11}$$

where α now denotes a set of $N-1$ states, $\alpha = \{\alpha_1, \cdots, \alpha_{N-1}\}$, all of which are different, and the sum $\sum'$ is over all possible permutations of N particle labels such that each particle appears only once in each term. Since the first sum in (2.11) contains terms involving only N-1 states, one of the electron variables is always missing in each term. On the other hand, the second sum includes all N electrons in each term so that pairs of electrons always occupy the same state. Therefore, this second sum can not affect the wave function which is already antisymmetrized, but is added here to satisfy (2.2). We also have

$$Q_\alpha = 1 - P_\alpha = \prod_{i=1}^{N} \delta(i - i') - P_\alpha . \qquad (2.12)$$

When P_α operates on a properly antisymmetrized function Ψ, we obtain

$$P_\alpha \Psi = (N!)^{-1/2} \det[\psi\alpha_1(1) \cdots \psi\alpha_{N-1}(N-1) \times u_\alpha(N)] \;, \qquad (2.13)$$

which contains an unknown function u_α of *one* variable; Eq. (2.13) should be compared with (2.9) which consists entirely of the basis functions ψ_n. The advantage of the Hartree-Fock form (2.9) is that the second function $P_{\alpha'}{}^{\mathrm{HF}}\Psi$, which is constructed in a similar way, is automatically orthogonal to $P_\alpha{}^{\mathrm{HF}}\Psi$, i.e., $P_{\alpha'}{}^{\mathrm{HF}} P_\alpha{}^{\mathrm{HF}} = \delta_{\alpha'\alpha} P_\alpha{}^{\mathrm{HF}}$. But the form (2.13) does not have such a nice property, and we have to construct the orthogonal function using the operator (2.12). However, the presence of u_α in (2.13) will make the function a little more flexible in many cases, especially when the Q_α part is added. It is also possible to construct other forms of projection operators, even within the restricted case being considered here. For example, a sum of products of N-2, as well as N-1 and N, single-particle operators gives a new P operator. The resulting $P\Psi$ will then contain an unknown function u of *two* variables, and such a function would be extremely difficult to obtain exactly, although the form may be just right to incorporate strong two-particle correlations.

B. Variation-Iteration Method

Once the specific forms of P_α and Q_α are chosen as given by (2.11) and (2.12), the solution of (2.3) proceeds as follows: We first solve the homogeneous equation of (2.3a).

$$P(H - E_0{}^P) P\Psi^P = 0 \;, \qquad (2.14)$$

where we put $P = P_\alpha$ for the simple case when P contains only one term P_α. After the N-1 variables are integrated over, and a particular angular momentum consistent with total J and S are taken, (2.3a) and (2.14) can be written in a typical form as

$$\left(\frac{d^2}{dr^2} - w(r) - \kappa^2 \right) u(r) = \int_0^\infty K(r, r') u(r') \, dr' + B(r). \qquad (2.15)$$

In (2.15), $\omega(r)$ is assumed to contain both the "static" potential and the centrifugal barrier term. $B(r)$ comes from $PHQ\Psi$ in (2.3a) and is absent in the case with (2.14). For given $B(r)$ and $K(r, r')$, (2.15) can be solved numerically exactly for all practical purposes, and this is the direct consequence of the simple form of P_α we have chosen.

By Green's theorem, we have from (2.14) and (2.3)

$$\Delta_0 = E_0 - E_0{}^P = (P\Psi^P ,\; PHQ\Psi)/(P\Psi^P ,\; P\Psi). \qquad (2.16)$$

It is convenient in discussing the iteration procedure to define further the subspaces of P as

$$P = \Pi + \Sigma, \qquad (2.17)$$

where $\Pi = P\Psi^P)(P\Psi^P ,\; P\Psi^P)^{-1}(P\Psi^P ,$

$$\Pi^2 = \Pi = \Pi^\dagger \,, \qquad (2.18)$$

$$\Sigma P = \Sigma, \qquad \Pi P = \Pi, \qquad \Sigma\Pi = 0.$$

We can rewrite (2.3a) in the form

$$\Pi(H - E_0)\Pi\Psi = -\,\Pi H Q \Psi \;, \qquad (2.19a)$$

$$\Sigma(H - E_0)\Sigma\Psi = -\,\Sigma H Q \Psi, \qquad (2.19b)$$

where (2.19a) is equivalent to (2.16) since Π operates in the full N-particle space and $(P\Psi^P, P\Psi) = (P\Psi^P, \Pi\Psi)$. Thus, (2.19) replaces (2.16) and (2.3a). [For the case with the Hartree-Fock basis,[5] extra terms of the form $-\Pi H \Sigma \Psi$ and $-\Sigma H \Pi \Psi$ appear in (2.19) due to the fact that the basis functions there do not commute with PHP.]

The variation-iteration procedure to solve (2.3) for the lowest state under consideration is given by the following three steps:

Step A: For given E_{0t} and $P\Psi_t$, $Q\Psi_t$ is obtained variationally by minimizing the quantity I as $\delta I = 0$, where

$$I\,[Q\Psi_t] = 2\,(Q\Psi_t , QHP\Psi_t) + (Q\Psi_t , [H - E_{0t}]\, Q\Psi_t). \qquad (2.20)$$

The trial function $Q\Psi_t$ in (2.20) is constructed to be orthogonal to $P\Psi_t$ and to satisfy the decaying boundary condition asymptotically. Variational parameters are contained in $Q\Psi_t$, but E_{0t} in (2.20) is held *fixed* during the variation.

Step B: Using $Q\Psi_t$ of step A, the energy correction Δ_{0t} is evaluated as

$$\Delta_{0t} = (P\Psi^P ,\; PHQ\Psi_t)/(P\Psi^P , P\Psi_t) \;, \qquad (2.21)$$

and the new energy value is given by

$$E_{0t} = E_0{}^P + \Delta_{0t} . \qquad (2.22)$$

Step C: The iteration cycle is completed by solving (2.19b) for $\Sigma\Psi_t$ exactly numerically using the new values of E_{0t} and $Q\Psi_t$, that is,

$$\Sigma(H-E_{0t})\Sigma\Psi_t = -\Sigma HQ\Psi_t, \tag{2.23}$$

or, more directly for $P\Psi_t$ with

$$P(H-E_{0t})P\Psi_t = -PHQ\Psi_t. \tag{2.23$'$}$$

Both (2.23) and (2.23′) are of the form (2.15) involving u of a single variable. The iteration cycle (A, B, C) may be started, for example, by taking initially $E_{0t}=E_0{}^P$ and $P\Psi_t = P\Psi^P$. Except for a few minor changes, the procedure given here is identical to that in the scattering theory.[2]

C. Convergence of Iteration Series and Extremum Property

For the above method to be effective, we require that $P\Psi^P$ of (2.14) be dominant by a proper choice of h^M and the operator P. The iteration is to make a small correction arising from the coupling of $P\Psi$ to $Q\Psi$, and thus, is expected to converge rapidly. We define formally

$$\begin{aligned} &\Sigma\Psi = G^{\Sigma}\Sigma HQ\Psi, \quad G^{\Sigma} = [\Sigma(E_0-H)\Sigma]^{-1}, \\ &Q\Psi = G^{Q}H\Pi\Psi + G^{Q}H\Sigma\Psi, \quad G^{Q} = [Q(E_0-H)Q]^{-1}, \end{aligned} \tag{2.24}$$

and obtain

$$\begin{aligned} P\Psi &= \Pi\Psi + G^{\Sigma}\Sigma HG^{Q}H\Pi\Psi + \mathcal{K}\Sigma\Psi \\ &= \Pi\Psi + \sum_{m=0}^{\infty} K^m(G^{\Sigma}HG^{Q}H\Pi\Psi), \end{aligned} \tag{2.25}$$

where $\mathcal{K} = G^{\Sigma}HG^{Q}H\Sigma$.

In the actual case, we have, of course, an approximate $\mathcal{K}_t$ rather than the exact $\mathcal{K}$,

$$\mathcal{K}_t = G^{\Sigma}{}_t HG^{Q}{}_t H\Sigma ,$$

where $G^{\Sigma}{}_t$ is still the exact "static" Green's function but for the approximate energy E_{0t}, while $G^{Q}{}_t$ is a variational approximation to G^Q as it is obtained from step B. If we assume that $\mathcal{K}-\mathcal{K}_t$ is negligible, then, since the kernel $\mathcal{K}$ is presumably compact, we have the convergence condition for the series (2.25) given by[2]

$$|\gamma_n| < 1 \tag{2.26}$$

for all n, where γ_n are the strength eigenvalues defined by

$$\mathcal{K}|\gamma_n\rangle = \gamma_n|\gamma_n\rangle .$$

Equation (2.26) implies that if E_{0t} initially is so crude that there are one or more states supported by the effective interaction $\Sigma HG^{Q}H\Sigma$ with energies below E_{0t}, then the iteration series (2.25) would diverge. Certainly such a situation is contrary to the assumption of the $P\Psi$ dominance. It is probably always possible to adjust h^M and P such that the effect of the Q space is minimal.

We now discuss the extremum property of the energy calculated. The upper bound $E_0 \leq E_{0t}$ can be shown trivially; for the trial function which has converged, we write

$$\Psi_t = \Pi\Psi + \Sigma\Psi_t + Q\Psi_t, \tag{2.27}$$

where $\Pi\Psi$ is the exact and uncoupled solution of (2.14) and where $\Sigma\Psi_t$ are given by (2.24) with G^{Σ} and G^{Q} replaced by their approximate forms. Direct substitution of (2.27) into the Ritz principle

$$\delta I_R = 0, \tag{2.28}$$

where $I_R[\Psi_t, \lambda_t] = (\Psi_t, H\Psi_t) + \lambda_t[1-(\Psi_t, \Psi_t)]$

gives, after some cancellations of terms and using Eqs. (2.20), (2.21), and (2.23),

$$I_R \to E_0{}^P(\Pi\Psi, \Pi\Psi) + \Delta_{0t}(\Pi\Psi, \Pi\Psi) + \lambda_t[1-(\Pi\Psi, \Pi\Psi)] \tag{2.29}$$

As λ_t is varied, (2.29) gives $\lambda_t = E_{0t}$ and this proves the upper bound. As in the scattering case, this upper bound results essentially from the fact that, for $E_0 \cong E_{0t}$, $G^{Q}{}_T \leq G^{Q}{}_t < 0$, or more precisely,

$$D^{-1} \leq Q\Psi_t)(Q\Psi_t, DQ\Psi_t)^{-1}(Q\Psi_t < 0, \tag{2.30}$$

where $D = Q(E_0 - H - HG^{\Sigma}H)Q$ and $G^{\Sigma} < 0$.

If the coupling between the Q and the P spaces is small, then the "shift" operator $QHG^{\Sigma}HQ$ is probably negligible and $D \approx Q(E_0 - H)Q < 0$. We note here that if E is not the lowest state, then the procedure should be modified to retain such inequality, (2.30).

The opposite, lower bound on E_0 can also be obtained in exactly the same way as in the scattering case.[2] Again assuming $E_{0t} \approx E_0$, we write

$$\begin{aligned} &DQ\Psi_t \equiv -R_t, \\ &DQ\Psi = QH\Pi\Psi \equiv -R . \end{aligned} \tag{2.31}$$

Since $(R_t, R_t) = J_t \geq 0$, we immediately have a formula equivalent to Temple's[6]:

$$E_0 \geqslant E_{0t} - J_t / [(Q\Psi_t,\ Q\Psi_t)(\mathcal{E}_1{}^Q - E_{0t})] \quad , \tag{2.32}$$

where $\mathcal{E}_1{}^Q$ is the lowest eigenstate of $-D$. The formula analogous to that of Stevenson and Crawford[7] can also be derived which involves the $J_t{}^{1/2}$ factor, but not $(\mathcal{E}_1{}^Q - E_{0t})^{-1}$. We refer to Ref. 2 for such formulas and their improvements.

III. EXAMPLES AND IMPROVEMENTS

In this section, we consider several specific applications and also possible improvements of the variation-iteration method (VIM). For the two- and three-electron atoms, we explicitly construct the projection operators, taking into account the spin symmetries. The method, however, may turn out to be more useful for atoms with many more electrons, as with the Hartree-Fock approach. Next we consider a problem in which Ψ_t obtained by VIM is used to evaluate the expectation value of an operator Ω. Here, a variational approach due to Schwartz[8] may be used to improve the calculation. Finally, VIM is modified in Sec. II C so as to be applicable to bound systems other than atomic systems in which heavy central cores are absent.

A. Two-Electron Atoms

For atoms with two electrons such as H^-, He, and Li^+, we have[9] simply, from (2.11)

$$\begin{aligned} &P_0(1,2) = P_0(1) + P_0(2) - P_0(1)P_0(2), \\ &Q_0(1,2) = Q_0(1)Q_0(2), \end{aligned} \tag{3.1}$$

and (for an infinitely heavy nucleus)

$$\begin{aligned} &[P_0(1), P_0(2)] = 0, \\ &P_0(1)Q_0(2) \neq 0. \end{aligned} \tag{3.2}$$

In actual problems with spins, we have the spatial part of the wave function given by

$$\Psi(1,2) = \sum_n [\psi_n(2)\bar{u}_n(1) + \epsilon\psi_n(1)\bar{u}_n(2)],$$

with $\epsilon = \pm 1$, and the sum includes also the continuum states of the complete set $\{\psi_n\}$. With $P = P_0$ and $Q = Q_0$, for simplicity, we have

$$\begin{aligned} P\Psi = \psi_0(2)[\bar{u}_0(1) &+ \epsilon \sum_n \psi_n(1)(\psi_n(2), u_n(2)) \\ &- \epsilon\psi_0(1)(\psi_0(2), \bar{u}_0(2))] + \epsilon[1 \leftrightarrow 2] \\ \equiv \psi_0(2)u_0(1) &+ \epsilon\psi_0(1)u_0(2). \end{aligned} \tag{3.3}$$

Thus, $P\Psi$ contains the function u_0 of *one* variable which is to be evaluated exactly, and $P\Psi^P$ assumes the same form as (3.3) with u_0 replaced by $u_0{}^P$. Since $P\Psi^P$ and $P\Psi$ are obtained exactly from (2.14) and (2.23′) for given $Q\Psi_t$ and $E_{0t} \approx E_0$, the assumption of the P dominance means that the total wave function Ψ_t obtained by VIM will in general be more accurate than the ones obtained by a purely variational approach. Because of the presence [9, 10] of the spurious solution $c\,\psi_0(1)\psi_0(2)$ in the case of the triplet state with the total orbital angular momentum $L = 0$, some care is necessary in setting up a numerical program for (2.14) and (2.23′), but this problem is not expected to be serious.

The accuracy of $P\Psi_t$ can further be improved by enlarging the P space. $P = P_0(1,2)$ of (3.1) gives a single integrodifferential equation for u_0. We may take instead a finite subset of $P_n(i)$ and construct a single-particle operator of the form

$$P^S(i) = \sum_{m=0}^{s} P_m(i), \tag{3.4}$$

where S denotes a subset of $s+1$ states, $S = \{\psi_0, \psi_1, \ldots, \psi_s\}$. A more general two-particle operator can be constructed now as

$$P = P^S(1,2) = P^S(1) + P^S(2) - P^S(1)P^S(2) \tag{3.5}$$

and $$Q = Q^S(1,2) = 1 - P^S(1,2) = Q^S(1)Q^S(2). \tag{3.6}$$

They satisfy, aside from (2.2),

$$\begin{aligned} &P_m(i)P^S(i) = P_m(i) \quad , \quad \text{where } m \in S \\ &[Q_m(i), P^S(j)] = 0 \quad . \end{aligned} \tag{3.7}$$

With (3.5), the P equations (2.23′) form a set of $s+1$ coupled integrodifferential equations for the functions $u_n(i)$, $n = 0, 1, \cdots, s$. For s not too large, in the order of 10 or less, such solutions can be obtained on a computer.

In connection with the fine and hfs studies, there are already available [11–13] several extremely accurate calculations of the nonrelativistic energies and wave functions. It would be of interest, therefore, to test VIM for those states and to compare the result with the more accurate analyses.

B. Three-Electron Atoms

The case of three-electron atoms illustrates nicely the reasons for choosing (2.11). Again, (2.11) is only partially correct since in it we neglected the spin degrees of freedom. In fact, we can put two of the three electrons in the 1s state of h^M, for example, and write the P operator as

$$P_0(i,j)=P_0(i)+P_0(j)-P_0(i)P_0(j) \tag{3.8}$$

for $i,j=1$, 2, and 3 but $i\neq j$, and

$$[P_0(i),P_0(j)]=0,$$

$$[P_0(i),P_0(j,k)]=0.$$

We try first the form

$$P_0(1,2,3)=P_0(1,2)+P_0(3)-P_0(1,2)P_0(3)$$
$$=\sum_{i=1}^{3} P_0(i)-\sum_{i<j}^{3} P_0(i)P_0(j)+\prod_{i=1}^{3} P_0(i), \tag{3.9}$$

$$\text{and}\quad Q_0(1,2,3)=1-P_0(1,2,3)=\prod_{i=1}^{3} Q_0(i). \tag{3.10}$$

As discussed earlier, (3.9) gives rise to $P\Psi$ (and $P\Psi^P$), which contains a function u of two variables, and thus is not readily calculable in general although it may be for some special cases, and then the resulting $P\Psi$ may be a much better approximation than the one involving a function u of one variable.

A much simpler form would be

$$P=P_0(1,2,3)=\sum_{i>j}^{3} P_0(i)P_0(j)-2\prod_{i=1}^{3} P_0(i), \tag{3.11}$$

$$\text{and}\quad Q=Q_0(1,2,3)=\prod_{i=1}^{3}\delta(i-i')-P_0(1,2,3)$$
$$=\prod_{i=1}^{3} Q_0(i)+\sum_{i=1,\,(j\neq i\neq k)}^{3}\sum_{j>k} P_0(i)Q_0(j)Q_0(k). \tag{3.12}$$

They are obviously symmetric in all three particle coordinates and $P\Psi$ obtained with (3.11) contains u of only *one* variable. As in the two-electron atoms, P can be improved either by adjusting h^M or by adding more terms as was done in (3.5).

The discussion given above illustrates that VIM can be easily extended to atoms with many more electrons and the construction of P and Q is entirely a triviality. In this connection, it is interesting to note that neither the form (3.9) nor (3.11) would be acceptable for the e^- He scattering problem in the variational-bound approach, simply because such P would not give the correct asymptotic-state projection. To preserve the extremum property of the scattering parameters, the exact He wave function is required.

C. Expectation Value of Operators

Although we attempt by VIM to improve the over-all accuracy of the wave function, $Q\Psi_t$ is still obtained by the variational procedure (step B) and thus, may not be accurate enough as required in a particular problem. If we denote the error in the variational wave function Ψ_t by $\delta\Psi_t\equiv\Psi_t-\Psi$, it is well known that the variational energy E_{0t} is usually accurate roughly to the order $(\|\delta\Psi_t\|/\|\Psi\|)^2$. On the other hand, the expectation value of an operator Ω may be only accurate to the order $\|\delta\Psi_t\|/\|\Psi\|$. Schwartz[8] has discussed a method of improving $(\Psi_t, \Omega\Psi_t)$ and also Ψ_t itself, and we may apply it here to $Q\Psi_t$. Assuming that the variational energy is almost correct, the error in Ψ_t gives

$$(H-E_{0t})\Psi_t=\mathcal{R}_t, \tag{3.13}$$

which may be small, but not negligible. The variational statement for the expectation value of Ω is then given by[8]

$$[\Omega]=\frac{(\Psi_t,\Omega\Psi_t)+(\chi_t,\mathcal{R}_t)+(\mathcal{R}_t,\chi_t)}{(\Psi_t,\Psi_t)}, \tag{3.14}$$

where χ_t satisfies the equation

$$(H-E_{0t})\chi_t=\Omega\Psi_t-(\Psi_t,\Omega\Psi_t)\Psi_t/(\Psi_t,\Psi_t). \tag{3.15}$$

However, χ_t is not in general easy to obtain for complicated Ψ_t and Ω, and Schwartz has also given an alternative procedure: For a simpler function Ψ' with reasonably small $\delta\Psi'\equiv\Psi'-\Psi$, it may be possible to obtain χ' which satisfies (3.15) with Ψ' replacing Ψ_t. Then, with χ' in the place of χ_t in (3.14), we have $[\Omega]$ to the accuracy $\|\delta\Psi_t\|\cdot\|\delta\Psi'\|/\|\Psi\|^2$. This may still be an improvement so long as $\|\delta\Psi'\|/\|\Psi\|<1$. The entire error in Ψ_t of VIM comes essentially from $Q\Psi_t$. If we write, for $E_{0t}\approx E_0$,

$$Q(H-E_{0t})Q\Psi_t\equiv\mathcal{R}_t^{Q}, \tag{3.16}$$

then (3.13) gives, with (2.23′) and (3.16),

$$P\mathcal{R}_t=0, \tag{3.17a}$$

$$Q\mathcal{R}_t=\mathcal{R}_t^{Q}+QHP\Psi_t, \tag{3.17b}$$

where (3.17a) is, of course, a simple consequence of step C of the iteration cycle. Substitution of (3.17) into (3.14) should give the desired improvement. Incidentally, we note that the explicit evaluation of $\mathcal{R}_t^Q$ will also be useful in estimating the lower bound on E_{0t}, as discussed in Sec. II.

D. Absence of Heavy Cores

The commutativity (2.7) is the important simplifying feature of $P_m(i)$ used to formulate VIM and is a direct consequence of the presence of the infinitely heavy nucleus. It is a much more difficult task to construct the proper P if the core is not so heavy, as, for example, in mesic atoms and in nuclear bound-state problems. In general, we have $[P_m(i), P_n(j)] \neq 0$ for $i \neq j$, and the formalism of Sec. II is no longer applicable. We recognize, however, that the difficulty is very similar to that in the rearrangement collision theory, and a general formalism developed recently[14] may be applied to the present case. It is noted that the usual Hartree-Fock method based on the shell model of the nucleus ignores this problem completely. For simplicity, we consider a three-particle bound system with the particles 1 and 2 being identical, as in the triton and He^3. Assuming the central two-body interactions, we have

$$H = T + V_{12} + V_{13} + V_{23} , \qquad T = T_1 + T_2 + T_3 , \tag{3.18}$$

which we rewrite in the form

$$H = H_1 + V_1 = H_2 + V_2 ,$$

where $H_1 = T + V_{23}, \quad V_1 = V_{12} + V_{13}$,

$$H_2 = T + V_{13}, \quad V_2 = V_{21} + V_{23} .$$

Of course, to be completely consistent mathematically, the three-particle problem should be treated by the method developed by Faddeev,[15] Weinberg,[16] and others. But, for the bound-state problem involving projection operators,[17] it is not necessary to employ the full hierarchy of equations of the many-particle theory. We follow here the result of Ref. 14, and write

$$\Psi = \Psi_1 + \Psi_2 , \tag{3.19}$$

and define a model Hamiltonian

$$h_{23}^{M}(23) = t_{23}(23) + U_{23}^{M}(23) , \tag{3.20}$$

where $\quad T_2 + T_3 = T_{23} + t_{23}(23)$. $\qquad$ (3.20′)

In (3.20′), T_{23} is the kinetic-energy operator of the c.m. of the particles 2 and 3, and t_{23} is for their relative motion. As in Sec. II, we let

$$h_{23}^{M}(23)\psi_m^{1}(23) = \epsilon_m^{1}\psi_m^{1}(23),$$

and obtain $P_m^{1}(23) = \psi_m^{1}(23)\rangle\langle\psi_m^{1}(23)$,

$$Q_m^{1}(23) = 1 - P_m^{1}(23) . \tag{3.21}$$

Obviously, we have

$$[P_m^{i}, P_n^{j}] \neq 0 \tag{3.22}$$

for $i, j = 1, 2,$ and 3, but $i \neq j$. Substitution of (3.21) and (3.19) into (2.3) gives[14] the following set of coupled equations:

$$P_1[H_1 + Y_1 - E]P_1\Psi_1 = -P_1(V_2 - Y_2)P_2\Psi_2 - P_1(V_2 - Y_2)Q_2\Psi_2, \tag{3.23a}$$

$$P_2[H_2 + Y_2 - E]P_2\Psi_2 = -P_2(V_1 - Y_1)P_1\Psi_1 - P_2(V_1 - Y_1)Q_1\Psi_1, \tag{3.23b}$$

and similarly for $Q_i\Psi_i$. In (3.23), Y's are introduced to further minimize the effect of $Q\Psi$, but are otherwise quite arbitrary. (This may be an important advantage in actual applications and is not present in the Faddeev formulation.) For the case in which the particles 1 and 2 are identical, (3.23a) and (3.23b) degenerate to an identical form, and we have to solve only one of them. VIM can be applied to (3.23) and the corresponding equations for $Q\Psi$. We also note that in the case where the particle 3 is infinitely heavy, (3.23) reduces to the case with (3.1) for $Y_1 = Y_2 = 0$. The proof is straightforward.

ACKNOWLEDGMENT

The author would like to thank Professor G. Breit for the hospitality extended to him at Yale University and at State University of New York at Buffalo, and for several helpful suggestions for the improvement of the paper.

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[*] Work supported by the U.S. Atomic Energy Commission (NYO-4022-2).

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PHYSICAL REVIEW VOLUME 187, NUMBER 1 5 NOVEMBER 1969

Molecular-Beam Maser for the Shorter-Millimeter-Wave Region: Spectral Constants of HCN and DCN†

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(Received 2 July 1969)

A millimeter-wave molecular-beam maser has been made to operate as both an amplifier and an oscillator on the $J=1\rightarrow 0$ and the $J=2\rightarrow 1$ transitions of HCN at 88.6 and at 177.2 kMc/sec, respectively, thus doubling the previously operational frequency range of such masers. With this maser, hyperfine components of these transitions have been measured for $H^{12}C^{14}N$ and $D^{12}C^{14}N$ to nine significant figures. The spectral constants (in kc/sec) that are derived from these frequencies are, for HCN, $B_0=44\,315\,975.7\pm0.4$, $D_J=87.24\pm0.06$, $(eQq)_N=-4709.1\pm1.3$, and $C_N=10.4\pm0.3$; for $D^{12}C^{14}N$, $B_0=36\,207\,462.7\pm0.2$, $D_J=57.83\pm0.04$, $(eQq)_N=-4703.0\pm1.2$, $C_N=8.4\pm0.3$, $(eQq)_D=194.4\pm2.2$, and $C_D=-0.6\pm0.3$.

INTRODUCTION

Molecular-beam techniques provide the highest resolution and make possible the most accurate measurement of molecular spectral frequencies of any known method. Although the beam maser was first successfully operated[1] in 1954, it has, to date, been used to measure the spectral transitions of only a few molecules, notably the inversion spectrum of ammonia, NH_3, and NH_2D, and rotational transitions of the asymmetric-top molecules H_2O, HDO, D_2O, HDS, HDSe, H_2CO, and HDCO. These transitions all occur in the centimeter-wave region. There are several reasons for this. Microwave techniques become increasingly more difficult as they are extended into the millimeter and submillimeter region, and detection sensitivity decreases rapidly. Maser techniques require transitions with relatively large populations and favorable state-selection properties. Both of these are provided by the above types of molecules. Linear and symmetric-top molecules without inversion result in either poor population (molecules with small rotational constants) or transitions outside the centimeter region (molecules with large rotational constants). The state selection is also most effective for the closely spaced doublets of the NH_3 inversion spectrum and of the light asymmetric molecules.

Two molecular-beam masers have previously been made to operate in the millimeter-wave region. Marcuse[2] succeeded in obtaining maser action, both amplification and oscillation, with the $J=1\rightarrow 0$ rotational transition of HCN at 88.6 kMc/sec, but he did not make high-precision measurements of the frequencies. Likewise, Krupnov and Skvortsov[3] constructed a molecular-beam maser which operated successfully on the $1_{01}\rightarrow 0_{00}$ transition of H_2CO at 72.8 kMc/sec, but they did not, to our knowledge, measure the spectral frequencies.

We have constructed an HCN beam maser which operates as amplifier and oscillator, not only on the hyperfine transitions of the $J=1\rightarrow 0$ transition, but also on the $J=2\rightarrow 1$ hyperfine transitions which fall at 177.2 kMc/sec. Thus we have succeeded