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# Effects of Approximate Cluster Functions on Scattering Parameters and an Improved Pseudostate Expansion for Many-Particle Scattering

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The effects on scattering parameters of approximate cluster functions which appear in the asymptotic boundary conditions are examined by a model calculation of the elastic electron-hydrogen scattering. It is shown that (i) the resonance energies calculated with functions which are orthogonal to the approximate open-channel functions could be spurious, (ii) the phase shifts could deviate from the correct values as much as the relative error in the cluster functions, and (iii) the threshold mismatch may cause an enhancement of phase shifts. An improved pseudostate expansion is studied in which the prediagonalization of the cluster energy matrix is emphasized. This is seen not only to improve the threshold energies and incorporate the effect of the continuum states, but also to *optimize* the input functions in a given calculation. An additional diagonalization of the closed-channel energy matrix provides a set of quasistates for the resonance and distortion potentials.

## I. INTRODUCTION

In a composite-system scattering involving many particles, the asymptotic boundary conditions require an exact set of open-channel cluster functions, which are often difficult to evaluate. Such bound-state functions are either not available in many cases except in very crude forms, or too cumbersome to use in practice even if more accurate forms are available. Although there have been many theoretical attempts to estimate the atomic and molecular cross sections using a variety of crude functions, the extent to which approximate cluster functions affect the resulting scattering parameters is not very well understood. Furthermore, many of the theoretical methods available are formulated with the assumption that the asymptotic boundary conditions can be imposed on the scattering function exactly. Therefore, it is of considerable practical importance to obtain first a more quantitative estimate of the effect before elaborate calculations are to be carried out.

As the scattering parameters depend on the cluster functions in a very complicated way, we study the problem by an explicit model calculation in the case of elastic scattering of electrons (and positrons) by atomic hydrogen, for which many useful parameter values are available for ready comparison. The phase shifts in this case depend strongly on the static potential and exchange kernel, which are in turn very sensitive to the target functions being used. As the ground-state function is modified gradually from its exact form, we can watch the way the phase shift deviates from its correct value. The result of the calculation summarized in Sec. II strongly suggests the obvious fact that one cannot expect to obtain reliable amplitudes without improving the cluster functions. In particular, the existing theories can produce results which are totally unreliable. (See the positron solutions in Sec. II.)

In Sec. III, we consider an improved formulation of the pseudostate expansion, in which the *prediagonalization* of the cluster energy matrix (PCEM) is emphasized.[1,2] When the exact bound-state functions for the open channels are available, as in the $e^+$-H and $e^-$-H scattering, the procedure is merely a convenient device to ease the computational problem.[3,4] However, when such functions are available only in approximate forms, the above procedure seems to be essential in order to obtain physically reasonable amplitudes, as our study will show. More importantly, the PCEM allows one to *optimize* the calculation in the following sense. When the open- and closed-channel components are treated separately in deriving a set of scattering equations, one is likely to waste unnecessary calculational effort in treating one part of the problem more accurately than the other without knowing of course whether the result will improve. The PCEM produces not only the set of closed-channel basis functions which are orthogonal to all the open-channel functions, but also simultaneously improves the open-channel functions themselves, in accordance with the Hylleraas-Undheim (HU) theorem.[5] Aside from the known advantages of the pseudostate expansion which allows us to include the effect of many excited and continuum channels, the above feature is very essential in improving the amplitudes.

A general procedure is outlined in Sec. III which involves three main steps in the evaluation of scattering amplitudes, and the various useful features of each step are discussed in detail. Its application to our model problem is carried out to illustrate these points.

TABLE I. Properties of the approximate target functions $\psi_{0t}=N_0 e^{-ar}$, where $N_0=2a^{3/2}$. The function with $a=1.0$ is the exact $\psi_0$.

| $a(a_0)$ | $E_{0t}$(Ry) | $\gamma$ | $(\psi_{0t}/\psi_0)r=a^{-1}$ | $\lvert(E_{0t}-E_0)\rvert^{1/2}$ |
|---|---|---|---|---|
| 0.7 | −0.91 | 0.952 | 0.837 | 0.30 |
| 0.8 | −0.96 | 0.986 | 0.894 | 0.20 |
| 0.9 | −0.99 | 1.006 | 0.949 | 0.10 |
| 1.0 | −1.00 | 1.000 | 1.000 | 0.00 |
| 1.1 | −0.99 | 1.000 | 1.049 | 0.10 |
| 1.2 | −0.96 | 1.000 | 1.095 | 0.20 |

## II. MODEL STUDY—EFFECT OF APPROXIMATE CLUSTER FUNCTIONS

In order to study the effects of approximate target functions on the scattering parameters and to improve the theory of complex system scattering, we explicitly consider as a model the elastic scattering of electrons (and positrons) by atomic hydrogen, where the resonance structure and phase shifts are well known to great accuracy in the case of zero total partial-wave and singlet spin state. Thus, by solving the scattering problem with the slightly modified ground-state function $\psi_{0t}$ of hydrogen, we should be able to estimate the variation in the scattering parameters as $\psi_{0t}$ is changed. We limit the calculations to a necessary minimum by taking into account the excited states with only the zero relative angular momentum $l=0$ $(=l_1=l_2)$; the states with $l>0$ are not interesting for our purpose because they are automatically orthogonal to the correct target function $\psi_0$.

### A. Properties of Approximate Target Function

We start the model study by intentionally modifying the target function $\psi_0$ in the form

$$\psi_{0t}(r)=2a^{3/2}\,e^{-ar}\;,\quad(\psi_{0t},\psi_{0t})=1\;, \tag{2.1}$$

where the nonlinear scaling parameter $a$ will be varied around the exact value $a=1.0$ for $\psi_0(r)$. Here, we employ the units such that $m=\hbar=e^2=a_0=1$ and the energy is in rydbergs. The ground-state energy $E_{0t}$ corresponding to (2.1) is given simply by

$$E_{0t}=-a(2-a)=(\psi_{0t},h\,\psi_{0t})\;, \tag{2.2}$$

and the overlap of $\psi_{0t}$ and $\psi_0$ is

$$\gamma=(\psi_0,\psi_{0t})=8a^{3/2}(1+a)^{-3}\;. \tag{2.3}$$

Table I shows the values of $E_{0t}$, $\gamma$, and $\psi_{0t}$ at several sample points in $r$ for the various choices of $a$. As expected, we have, with $h\psi_n=E_n\psi_n$,

$$\|(\psi_{0t}-\psi_0)/\psi_0\|\sim|(E_{0t}-E_0)/E_0|^{1/2}\equiv\epsilon^{1/2}\;, \tag{2.4}$$

where the notation ~ implies the same order of magnitudes. On the other hand, the overlap $\gamma$ is such that

$$|\gamma-1|\sim\epsilon\;, \tag{2.5}$$

which, if it is model independent, could be a very useful information for improving the theory, as we will discuss in Sec. III.

For the sake of simplifying the notation, we define the approximate projection operators as

$$\begin{aligned}P_{1t}&=\psi_{0t}(r_1))(\psi_{0t}(r_1')\;,\\ Q_{1t}&=\delta(r_1-r_1')-P_{1t}\;,\end{aligned} \tag{2.6}$$

and

$$\begin{aligned}P_t&=P_{1t}+P_{2t}-P_{1t}P_{2t},\quad[P_{1t},P_{2t}]=0\;,\\ Q_t&=Q_{1t}Q_{2t}\;,\end{aligned} \tag{2.7}$$

for the full two-electron space. They are to be compared with the exact operators $P_t$, $Q_t$, $P$, and $Q$ defined in an analogous way.

### B. Resonance Energies and Distortion Potentials

As stated earlier, the model includes only the $l=0$ states in the $Q$ space for distortions. Then, the closed-channel Hamiltonian $QHQ$ supports one resonance state below the first excitation threshold[6] at the energy −0.2527 Ry. However, with our crude functions, we do not expect to produce this state, so that, in the following, we simply *assume* that such a state does not exist. (Certainly, we will find a state with much lower energy as $a$ is varied from $a=1.0$. Also, we do not find any states when $a=1.0$ is taken.)

With the states in the $Q$ space defined as

$$QHQ\,\Phi_n=E_n^{\,Q}\,Q\Phi_n\;,\quad n=1,2,\ldots \tag{2.8}$$

we have, for all $n$ (except the state we mentioned above),

$$E_n^{\,Q}\geqslant E_1\quad(l=0)\;. \tag{2.9}$$

Alternatively, by simultaneously diagonalizing the matrices $H_{mn}^{\,Q}$ and $N_{mn}^{\,Q}$ defined by

$$\begin{aligned}H_{mn}^{\,Q}&=(Q\Phi_{mt},QHQ\Phi_{nt})\;,\\ N_{mn}^{\,Q}&=(Q\Phi_{mt},Q\Phi_{nt})\;,\end{aligned} \tag{2.10}$$

we have, from the Hylleraas-Undheim theorem, the resulting eigenvalues $E_{nt}^{\,Q}$ satisfying the inequalities

$$E_{nt}^{\,Q}\geqslant E_n^{\,Q}\geqslant E_1\;. \tag{2.11}$$

However, if the operator $Q$ is not known and the approximate $Q_t$ of (2.7) is used instead, then the inequalities (2.11) need no longer be valid in general. The interesting question is then to what extent (2.11) will be violated as we replace the operator $Q$ by $Q_t$. To study this problem, we choose the trial functions of the form

$$Q_{it}\,\varphi_{nt}(r_i)=e^{-b_nr_i}-d_ne^{-ar_i}\;,\quad i=1\text{ and }2 \tag{2.12a}$$

TABLE II. One-term resonance energies corresponding to $Q_t H Q_t$ are given, together with the properties of the trial functions which are made orthogonal to the approximate target functions $\psi_{0t}$. Note the inequality $E_{1t} < E_1 = -0.25$ Ry for some sets of parameters, and also the spurious resonance at $a = 0.7$, $b = 0.3$.

| | $a$ | $H_{tt}^{Q}$ | $N_{tt}^{Q}$ | $E_{1t}^{Q(1)}$ | $h_{tt}$ | $n_{tt}$ | $E_{1t}$ |
|---|---|---|---|---|---|---|---|
| $b = 0.3$ | | | | | | | |
| | 0.7 | −3.880 | 14.22 | −0.2728 | −1.045 | 3.771 | −0.2772 |
| | 0.8 | −4.973 | 21.48 | −0.2315 | −1.208 | 4.635 | −0.2606 |
| | 0.9 | −5.647 | 28.65 | −0.1971 | −1.324 | 5.353 | −0.2473 |
| | 1.0 | −5.962 | 35.34 | −0.1687 | −1.407 | 5.944 | −0.2368 |
| | 1.1 | −6.023 | 41.36 | −0.1456 | −1.470 | 6.431 | −0.2285 |
| | 1.2 | −5.930 | 46.68 | −0.1270 | −1.518 | 6.832 | −0.2222 |
| $b = 0.6$ | | | | | | | |
| | 0.7 | 0.0000 | 0.0004 | −0.0401 | −0.0058 | 0.0204 | −0.2833 |
| | 0.8 | 0.0005 | 0.0048 | 0.0961 | −0.0148 | 0.0694 | −0.2132 |
| | 0.9 | 0.0041 | 0.0178 | 0.2278 | −0.0199 | 0.1334 | −0.1492 |
| | 1.0 | 0.0145 | 0.0415 | 0.3499 | −0.0185 | 0.2037 | −0.0910 |
| | 1.1 | 0.0350 | 0.0757 | 0.4623 | −0.0105 | 0.2751 | −0.0383 |
| | 1.2 | 0.0671 | 0.1187 | 0.5654 | 0.0032 | 0.3445 | 0.0094 |

where

$$d_n = 8a^3 (a+b)^{-3} \quad (d_n \rightarrow d_{\mathrm{orth}} \text{ in Table VI})$$

and

$$Q_t \Phi_{nt} = Q_{1t} \varphi_{nt}(1) Q_{2t} \varphi_{nt}(2) . \tag{2.12b}$$

The calculation of the corresponding matrix elements $H_{mn}^{Qt}$ and $S_{mn}^{Qt}$ is straightforward, and the resulting $E_{nt}^{Qt(N)}$ are given in Tables II and III for the parameter values

$$a = 0.7, 0.8, 0.9, 1.0, 1.1, \text{ and } 1.2 , \qquad b_1 = 0.3, \quad b_2 = 0.6, \text{ and } b_3 = 1.5 . \tag{2.13}$$

The superscript ($N$) denotes the order of the matrices being diagonalized. It is obvious that $E_{1t}^{Qt(2)}$ with $b = b_1$ and $b_2$ for $a = 0.8$ and 0.7, for example, have already violated the inequalities (2.11) with

$$E_{1t}^{Qt(2)} < E_1 = -0.25 \text{ Ry}. \tag{2.14}$$

This contradicts (2.9), which we know is true, and thus these states are *spurious* and nonphysical. For some of these cases, we also have from Table II that

$$E_{1t} < E_1 \tag{2.15}$$

as a direct consequence of the way we constructed the trial functions $Q_{tt} \varphi_{nt}$. Evidently, both features (2.14) and (2.15) are *closely related,* as they are caused by the approximate $\psi_{0t}$. If the correct $\psi_0$ is used, we know that neither (2.14) nor (2.15) can happen. This particular observation will be the basis of an improved theory discussed in Sec. III.

Incidentally, we have searched for the best three-function set that gives the lowest $E_{1t}^{Qt(3)}$ for the case $a = 0.8$, and have found

$$E_{1t}^{Qt(3)} = -0.2538$$

for the parameters $b = 0.3$, 0.6, and 1.0. This indicates that, although $\psi_{0t}$ is not exact and the state with $E_{1t}^{Qt(3)} < E_1$ is spurious, the value for $E_{1t}^{Qt}$ seems to converge to a definite limit other than $E_0$ as $N$ is increased. Such a pheonomenon, also observed earlier by Temkin and Bhatia,[6] was difficult to understand, because the $Q_t$ space contains a small component of $\psi_0$ and thus $Q_t H Q_t$ should have a part of the continuum corresponding to the $P$ space. We give in the Appendix a simplified argument for such a convergence behavior. We also show that the simple orthogonalization procedure adopted here would give a reasonable estimate of the resonance energy $E_1^{Q}$ if

$$\left| (E_1^{Q} - E_1)/(E_1 - E_0) \right| \gtrsim \epsilon . \tag{2.16}$$

We make one final remark on the way $E_{1t}^{Q}$ violates the inequality $E_{1t}^{Q} > E_1^{Q}$. As is clear from Tables II and III, the deviation of $\psi_{0t}$ from the exact $\psi_0$ does *not always* imply that the spurious state should appear. For example, $E_{1t}^{Q(3)}$ of Table III is above $E_1$ at $a = 1.2$ but below it for $a = 0.8$, although $\psi_{0t}$ in both cases are probably of the same accuracy.

TABLE III. The resonance energies obtained by 2×2 and 3×3 matrix diagonalizations. More spurious states are found, but $E_{nt}^{Q(N)}$ seem to converge to values close to $E_1$ as $N$ increases.

| $b$ | ($b_1 = 0.3$ and $b_2 = 0.6$) | | ($b_1 = 0.3$, $b_2 = 0.6$, and $b_3 = 1.5$) | | |
|---|---|---|---|---|---|
| $a$ | $E_{1t}^{Q(2)}$ | $E_{2t}^{Q(2)}$ | $E_{1t}^{Q(3)}$ | $E_{2t}^{Q(3)}$ | $E_{3t}^{Q(3)}$ |
| 0.7 | −0.2781 | 0.2073 | −0.2781 | 0.0796 | 3.8821 |
| 0.8 | −0.2517 | 0.3508 | −0.2527 | 0.1664 | 4.3582 |
| 0.9 | −0.2350 | 0.5025 | −0.2378 | 0.2625 | 4.8478 |
| 1.0 | −0.2240 | 0.6470 | −0.2288 | 0.3493 | 5.3360 |
| 1.1 | −0.2169 | 0.7822 | −0.2235 | 0.4269 | 5.8225 |
| 1.2 | −0.2126 | 0.9078 | −0.2208 | 0.4953 | 6.3021 |

TABLE IV. Static phase shifts for the electric-hydrogen scattering with $L=S=0$, and for the positron-hydrogen scattering with $L=0$, all at $k(a_0)=0.4$. $\Delta E_0$ is the energy mismatch because of $E_{0t}\neq E_0$, and the corrected wave number $k'$.

| | | $e^-H(L=0=S,\ l=0)$ | | $e^+H(L=0)$ | |
|---|---|---|---|---|---|
| $a$ | $k'$ | $\delta^P(\Delta E_0=0)$ | $\delta^P(\Delta E_0\neq 0)$ | $\delta^P(\Delta E_0=0)$ | $\delta^P(\Delta E_0\neq 0)$ |
| 0.7 | 0.26 | 1.401 | 1.827 | −0.605 | −0.345 |
| 0.8 | 0.35 | 1.318 | 1.455 | −0.303 | −0.268 |
| 0.9 | 0.39 | 1.245 | 1.274 | −0.255 | −0.248 |
| 1.0 | 0.40 | 1.237 | 1.237 | −0.218 | −0.218 |
| 1.1 | 0.39 | 1.280 | 1.313 | −0.189 | −0.183 |
| 1.2 | 0.35 | 1.342 | 1.484 | −0.165 | −0.144 |

It seems that if $\psi_{0t}$ happens to have a larger curvature ($a=1.2$ case), then the resulting orthogonal function $\varphi_{nt}$ will have a larger kinetic energy contribution and thus a higher $E_{1t}{}^Q$.

### C. Scattering Phase Shifts

The effect of $\psi_{0t}$ on the phase shifts for a composite-system scattering is much more difficult to estimate, as $\psi_{0t}$ is involved in a highly nonlinear way. We study the problem here by solving the model, first in the exchange-static approximation (ESA) at $k=0.4$, and later adding the distortion terms corresponding to the $Q_t$ space.

In the ESA, the effect of $\psi_{0t}$ appears at two points; first, the static potential and the exchange kernel are modified when $a\neq 1.0$, and, second, the approximate target energy $E_{0t}\neq -1.0$ causes a threshold mismatch, with

$$\Delta E_0=E_{0t}-E_0=a(a-2)+1\ . \tag{2.17}$$

The equation we have to solve in the ESA is given by

$$\left(-\frac{d^2}{dr^2}+V_{00}(r)-E_0{}'+\Delta E_0\right)u_{0t}{}^P(r)$$
$$=-4a^3e^{-ar}\int_0^\infty ds\,e^{-as}[(2a-2)(r+s)$$
$$-(3a^2+E_0'-2a-\Delta E)sr+2rs/r_>]u_{0t}{}^P(s)\ , \tag{2.18}$$

with

$$V_{00}=-2e^{-2ar}(a+1/r)\ ,\qquad E_0{}'=E-E_0\ ,$$

and the distortion term is added to the right-hand side of (2.18) to give $\delta_s$, which is of the form

$$-2f(r)(f,u_{0t})/E_{QP}\ , \tag{2.19}$$

where

$$f(r)=(e^{-br}-de^{-ar})\,r\,\Gamma(r)\ ,$$
$$r\Gamma(r)=N_0(2a-2)\,r\left(\frac{1}{(a+b)^2}-\frac{d}{(2a)^2}\right)$$
$$-2N_0\frac{e^{-(b+a)r}}{(a+b)^3}[(a+b)r+2]$$
$$+2N_0d\,\frac{e^{-2ar}}{(2a)^3}(2ar+2)+\frac{4N_0}{(a+b)^3}-\frac{4N_0d}{(2a)^3}\ ,$$
$$E_{QP}=N_0{}^2(E-E_{1t}{}^{Q_t(1)})^{-1}\ .$$

Table IV contains the result of the phase-shift calculation in the ESA, either with $\Delta E_0$ retained or with $\Delta E_0$ arbitrarily set equal to zero. Although $\Delta E_0=0$ seems to be physically more reasonable, its real effect has never been estimated. In the $e^-$-H case, $\Delta E_0=0$ seems to improve the phase shifts, but this turned out to be accidental, as is clear from the $e^+$-H case shown also in the Table IV. However, the phase shifts calculated with $\Delta E_0\neq 0$ are consistently higher than that with $\Delta E_0=0$ for $k=0.4$. We note that, in this region of $k$, the correct phase shift decreases as a function of $k$, so that the above behavior is expected. In the region where the phase shift increases with $k$, as for example at very small $k$ in many cases, the above trend will probably reverse. The absolute deviations of $\delta^P$ from that of $\delta^P(a=1.0)$ are large, of the order of $\epsilon^{1/2}$ but the relative fluctuations are even larger when $\delta^P$ are small, as in the $e^+$-H case.

The effect of distortions caused by the coupling of the $P_t$ component to the $Q_t$ channels is shown by the phase shifts $\delta_s$ in Table V, again for both cases with $\Delta E_0=0$ and $\Delta E_0\neq 0$, and for $b_1$ and $b_2$. We have included in this calculation just one (nonlocal, separable) term to obtain only a crude estimate. As expected, we have the rigorous bound property at $a=1.0$:

$$\delta_s\geqslant\delta^P\quad\text{for}\quad E_{1t}{}^Q>E\ . \tag{2.20}$$

For the cases considered here, $E_{1t}{}^Q$ always lie above $E$, so that (2.20) seems to be satisfied in every case, but the differences $\delta_s-\delta^P$ vary appreciably as the values for $a$ are changed. This further indicates the fact that the difficulty with $\psi_{0t}$ is certainly not localized to the static part alone, but also persists in the effect of the $Q$ space. For $E_{1t}>E_1$, we more or less expect that (2.20) will be valid for some values of $a$ near 1.0, but as $a$ deviates from the correct value and as the number of terms in the

TABLE V. The "improved" phase shifts in which the distortion effect of the $Q_t$ space is included by a one-term trial function in the $l=0$ state. We have here $\delta_s>\delta^P$ rigorously if all the other parameters $(a, b, \Delta E_0)$ are the same, because we have $E_{1t}{}^Q>E$.

| $b$ | 0.3 | 0.3 | 0.6 | 0.6 |
|---|---|---|---|---|
| $a$ | $\delta_s(\Delta E_0=0)$ | $\delta_s(\Delta E_0\neq 0)$ | $\delta_s(\Delta E_0=0)$ | $\delta_s(\Delta E_0\neq 0)$ |
| 0.7 | 1.691 | 2.104 | 1.558 | 1.902 |
| 0.8 | 1.399 | 1.524 | 1.325 | 1.458 |
| 0.9 | 1.250 | 1.279 | 1.251 | 1.282 |
| 1.0 | 1.241 | 1.241 | 1.256 | 1.256 |
| 1.1 | 1.319 | 1.349 | 1.303 | 1.332 |
| 1.2 | 1.451 | 1.574 | 1.373 | 1.501 |

diagonalization increase, some of the $E_{nt}{}^{Q}$ will go down below the threshold $E_1$ and become spurious, and (2.20) will be violated as $E$ increases.

## III. IMPROVED THEORY OF MANY-PARTICLE SCATTERING

We consider in this section an improved procedure which could eliminate some of the difficulties discussed in Sec. II in terms of our model. The approach is essentially that given earlier[2] in connection with the single-particle formulation of the electron-atom scattering. We give here in more detail the various steps involved in the calculation of scattering amplitudes.

### A. General Formalism

The theory involves essentially three steps, which we discuss in terms of our model for simplicity. The Hamiltonian for the $e^-$-H system is given by

$$H = h(1) + h(2) + V_{12}\,, \qquad h(1) = -\nabla_1{}^2 - 2/r_1\,, \tag{3.1}$$

and we now consider the elastic scattering (single channel).

#### 1. *Prediagonalization of Cluster Energy Matrix*

As shown in detail in Sec. II, a mere orthogonalization of the $Q$-space trial functions to an approximate target function is not sufficient to prevent the spurious resonance states from occurring below the $E_1$ threshold. One obvious method to avoid this difficulty is to apply the HU theorem and diagonalize the energy matrix for $h$. Thus, for an arbitrary set of trial functions $\varphi_{it}$ which are square integrable, we construct the matrices

$$h_{ij} = (\varphi_{it}, h\varphi_{jt}) \text{ and } n_{ij} = (\varphi_{it}, \varphi_{jt})\,. \tag{3.2}$$

A simultaneous diagonalization of $h_{ij}$ and $n_{ij}$ gives an orthonormal set of functions $\{\psi_{nt}\}$ and $\{E_{nt}{}^{D}\}$, where

$$\psi_{nt} = \sum_{i=0}^{N} a_{ni}{}^{T} \varphi_{it}\,, \text{with } (\psi_{nt}, \psi_{mt}) = \delta_{nm} \tag{3.3}$$

and where $a_{ni}$ are the elements of the matrix which diagonalizes $h$ and $n$.

The set $\{\psi_{nt}\}$ has the following useful properties: (a) By the HU theorem, we have $E_{nt}{}^{D} \geqslant E_n$ for all $n \geqslant 0$. (b) Both $E_{nt}$ and $\psi_{nt}$ are improved, compared to the original $\varphi_{it}$. (c) The continuum states of $h$ are now properly included. (d) If any of the $\varphi_{it}$ are exact eigenfunctions of $h$, then $a_{ij} = 0$ for that $i$ and $j \neq i$. (e) The diagonalization above simplifies the coupled-channel calculation as was noted by Perkins[3] and by Burke *et al.*[4] in the pseudostate expansions. (f) The set $\{\psi_{nt}\}$ essentially defines the extent of the entire calculation, as we are to write

$$\Psi \to \Psi_t = \mathcal{a} \sum_{n=0}^{N} \psi_{nt}(1)\, u_n(2)\,, \tag{3.4}$$

where $\mathcal{a}$ is a proper symmetrizer. As noted earlier, we have made the optimum use of all $\varphi_{it}$, $i = 0, 1, 2, \ldots, N$, in generating the improved set $\{\psi_{nt}\}$. This then implies that in the original Hamiltonian $H$ we are replacing $h$ by

$$h(1) \to h_t(1) = \sum_{n=0}^{N} \psi_{nt})\, E_{nt}{}^{D}\, (\psi_{nt}\,. \tag{3.5}$$

In the notation of Sec. II, we write

$$h_t = P_{1t} E_{0t}{}^{D} + \sum_{n=1}^{N} E_{nt}{}^{D} P_{1,\,nt}\,, \tag{3.6}$$

where

$$P_{1,\,nt} = \psi_{nt}(1))\,(\psi_{nt}(1')\,, \quad n \neq 0\,.$$

#### 2. *Resonances and Distortion Potentials*

We may rewrite $\Psi_t$ in the form

$$\Psi_t = P_t \Psi_t + Q_t \Psi_t \tag{3.7}$$

for the open- and closed-channel components. Again, we construct the matrices in the full particle space as

$$\begin{aligned} H_{mn}{}^{Q} &= (Q_t \Phi_{mt}, H Q_t \Phi_{nt})\,, \\ N_{mn}{}^{Q} &= (Q_t \Phi_{mt},\, Q_t \Phi_{nt})\,, \end{aligned} \tag{3.8}$$

where[2]

$$Q_t \Phi_{nt} = \mathcal{a}\, \psi_{nt}(1)\, v_{nt}(2)\,. \tag{3.8$'$}$$

A simultaneous diagonalization of $H_{mn}{}^{Q}$ and $N_{mn}{}^{Q}$ then gives the eigenvalues and eigenfunctions

$$E_{nt}{}^{Q(N)} \text{ and } Q_t \Phi_{nt}{}^{Q(N)}\,,$$

where $Q_t \Phi_{nt}{}^{Q(N)}$ are linear combinations of the original $Q_t \Phi_{nt}$. From the scattering equation for $\Psi$, we can show that

$$Q_t \Psi_t = \sum_{n=1}^{N} Q_t \Phi_{nt}{}^{Q(N)} (Q_t \Phi_{nt}{}^{Q(N)}, H P_t \Psi_t)/(E_t - E_{nt}{}^{Q(N)})\,, \tag{3.9}$$

where $E_t$ is the adjusted total energy given by $E_t \equiv E_{0t}{}^{D} + E_0{}'$, that is $\Delta E_0 = 0$.

Obviously, some of the $E_{nt}{}^{Q(N)}$ may correspond to resonance states when they lie below the $E_{1t}{}^{D}$ threshold. (In our model, with $l = 0$, we expect none.) However, this identification cannot be made in a unique way since we are unable to prove rigorously that $E_{nt}{}^{Q(N)}$ thus obtained here provide upper bounds on the correct eigenstates of $QHQ$, i.e., $E_n{}^{Q}$. However, the calculation to be given at the end of Sec. III C strongly suggests that these $E_{nt}{}^{Q(N)}$ are much more reliable. (The possibility that some $E_{nt}{}^{Q(N)}$ are spurious is not entirely ruled out.) As in the method by Gailitis,[7] the rest of the terms in (3.9), other than the resonances near $E$, provide a smoother distortion potential.

#### 3. *Scattering Amplitudes*

The last step in our procedure is to solve for

$P_t \Psi_t$ and obtain the scattering parameters from the equations[8]

$$P_t (H - E_t) P_t \Psi_t = - P_t H Q_t \Psi_t \, , \qquad (3.10)$$

or, using (3.9),

$$P_t (H + W_t - E_t) P_t \Psi_t = 0 \, , \qquad (3.11)$$

where

$$W_t = \sum_{n=1}^{N} P_t H Q_t \Phi_{nt}{}^{Q}) (E_t - E_{nt}{}^{Q(N)})^{-1} (Q_t \Phi_{nt}{}^{Q}, HP_t \, . \qquad (3.12)$$

For $E_t < E_{nt}{}^{Q(N)}$, we have obviously

$$W_t < 0 \, . \qquad (3.13)$$

We may solve in general the coupled set of equations (3.11) by two different methods. As in the closed-coupling method, (3.11) can be solved exactly numerically. However, for a crude $P_t$, $Q_t$, and $W_t$, it is not again clear whether such an effort is necessary. Since the complicated part of the scattering is already contained in $W_t$, it may sometimes be more convenient to solve (3.11) by a variational procedure of the Kohn[9] or Harris type.[10] We have already considered such a procedure in the form of the quasiminimum principle,[11] and it can be extended here to the case when $P$ and $Q$ are not known exactly.

As with $E_{nt}{}^{Q(N)}$, it is not clear whether the solution of (3.11) would provide rigorous bounds on phase shifts; we are unable to give a formal proof here. However, the calculation to be described below indicates that if $\psi_{0t}$ is "accurate enough" compared with the $Q_t \Psi_t$, we may expect to have at least an approximate bound property.

This completes the discussion of the formal properties. Incidentally, in connection with the bound properties, we note that the Kato identity can be written as

$$(\lambda - \lambda_t)(\psi_{0t}, \psi_0) = (\Psi, (H - E)\Psi_t) \, , \qquad (3.14)$$

where

$$\lambda = - 2\pi\hbar^2 ab/m \, , \quad a = \text{initial amplitude}, \quad b = Ka \, ,$$

where $K$ is the reaction matrix. The right-hand side may be written as

$$(\Psi, (H - E)\Psi_t) = (\Psi_t, (H - E)\Psi_t) - (\Omega, (H - E)\Omega) \, , \qquad (3.15)$$

where

$$\Omega \equiv \Psi_t - \Psi \, .$$

First of all, we have seen in Sec. II that, at least in our model, the overlap can be very small. Now, we further assume that $E_{0t}{}^{D} \approx E_0$ for an accurate $\psi_{0t}$; then both terms in the right-hand side of (3.15) are finite. Under these circumstances, the minimum principle[12] follows just as before if we *strictly* impose the equalities $(\psi_0, \psi_{0t}) \cong 1$ and $E_{0t}{}^{D} \cong E_0$ throughout the calculation. (Otherwise the bound property breaks down because the coefficients multiplying the difference $E_{0t} - E_0$ are often infinite.)

We can now compare the procedure outlined above with those of others. The possible advantage of the prediagonalization of the cluster matrix has been known for sometime[1,2] in connnection with the continuum shell model. As a modified procedure of the variational bound formulation, the pseudostate expansion has been considered by Perkins[3] and also by Burke, Gallaher, and Geltman.[4] Although they also diagonalized the matrix to obtain the set $\psi_{nt}$, its effect in the case when the open-channel functions are not available in exact forms has never been investigated. On the other hand, the calculation carried out by Burke, Cooper, and Ormonde[13] for the electron-helium scattering in the close-coupling approximation comes closest to the present procedure in that the open- and closed-channel functions used there are calculated exactly from *one* single equation in the ESA[14]; thus they are mutually orthogonal and its energy matrix is diagonal. However, some of the higher excited states are not included in their calculation.

### B. Improved Model Calculation

We now apply the above procedure to our model. As a first step, we diagonalize the hydrogen energy matrix formed by a set of trial functions

$$\begin{aligned} &\varphi_0(r) = e^{-ar} \, , \qquad a = 0.7 - 1.2 \, , \\ &\varphi_i(r) = e^{-6_i r} \, , \quad b_1 = 0.3 \, , \quad b_2 = 0.6 \end{aligned} \qquad (3.16)$$

which gives an orthonormal set $\{\psi_{nt}{}^{D}\}$ and the energies $E_{nt}{}^{D}$, where the superscript $D$ denotes the diagonalized quantities. Thus we have, for example, with $N = 1$,

$$\begin{aligned} \psi_{0t}{}^{D} &= U_{00}\varphi_0 + U_{01}\varphi_1 = U_{00}(\varphi_0 - c\varphi_1) \, , \\ \psi_{0t}{}^{D} &= U_{10}\varphi_0 + U_{11}\varphi_1 = U_{11}(\varphi_1 - d_D\varphi_0) \, . \end{aligned} \qquad (3.17)$$

The values of $d_D$ are listed in Table VI, and are to be compared with $d_{\text{orth}}$. The resulting $E_{nt}{}^{D}$ for a $2\times 2$ matrix diagonalization are given in Table VI. Unlike in the case of simple orthogonalization of $\psi_{1t}$ to $\varphi_0$, both $E_{0t}{}^{D}$ and $E_{1t}{}^{D}$ are improved and satisfy $E_{nt}{}^{D} > E_n$, as expected, while we saw in Sec. II that these inequalities are not always valid for $E_{nt}$. The choice $b = 0.3$ seems to improve $E_{1t}{}^{D}$ more, while $b = 0.6$ contributes more to $E_{0t}{}^{D}$. Since $\psi_0$ is extremely simple in our model, we have a good improvement by a $2\times 2$ diagonalization, but we expect this to be more or less the case with other problems as well.

The second step involves a diagonalization of the $Q_t H Q_t$ matrices. Instead, we simply evaluated the expectation value and calculated $E_{1t}{}^{QD}$ using $\psi_{1t}{}^{D}$ above for different combinations of $a$ and $b$. Unlike

TABLE VI. Improved target energies by the diagonalization procedure (denoted by superscript $D$) which satisfy $E_{nt}{}^D > E_n$ in acdordance with the Hylleraas-Undheim theorem. The improved basis set is used to evaluate the resonance energies $E_{nt}{}^{QD}$, which seem to satisfy $E_{nt}{}^{QD} > E_n{}^Q > E_1$.

| | $a$ | $E_{0t}{}^D$ | $E_{1t}{}^D$ | $E_{1t}{}^{QD}$ | $d_{\text{orth}}$ | $d_D$ |
|---|---|---|---|---|---|---|
| $b=0.3$ | | | | | | |
| | 0.7 | −0.9415 | −0.2456 | −0.2280 | 2.75 | 2.25 |
| | 0.8 | −0.9740 | −0.2466 | −0.2160 | 3.08 | 2.65 |
| | 0.9 | −0.9935 | −0.2438 | −0.1969 | 3.37 | 3.10 |
| | 1.0 | −1.0000 | −0.2368 | −0.1687 | 3.64 | 3.64 |
| | 1.1 | −0.9937 | −0.2248 | −0.1284 | 3.88 | 4.30 |
| | 1.2 | −0.9753 | −0.2069 | −0.0709 | 4.09 | 5.09 |
| $b=0.6$ | | | | | | |
| | 0.7 | −0.9817 | −0.2114 | −0.0206 | 1.25 | 1.20 |
| | 0.8 | −0.9922 | −0.1809 | 0.0776 | 1.50 | 1.42 |
| | 0.9 | −0.9981 | −0.1410 | 0.2000 | 1.73 | 1.67 |
| | 1.0 | −0.0000 | −0.0910 | 0.3499 | 1.95 | 1.95 |
| | 1.1 | −0.9984 | −0.0300 | 0.5318 | 2.17 | 2.27 |
| | 1.2 | −0.9939 | 0.0433 | 0.7497 | 2.37 | 2.65 |

in the case with $E_{1t}{}^{Q(N)}$ of Tables II and III, we have found none of the cases with $E_{1t}{}^{QD} < E_1$. This is a big improvement over the simple orthogonalization procedure of Sec. II. [The $Q_t\Phi_{1t}$ used here are simply $\varphi_{1t}{}^D(1)\,\varphi_{1t}{}^D(2)$.] However, we are not able to show formally that $E_{1t}{}^{QD} > E_1$ in a rigorous sense. The comparison in Table VI between $d_{\text{orth}}$ of (2.12) and $d_D$ of (3.17) is also interesting. Using the improved $\psi_{0t}{}^D$, we have recalculated the phase shifts in the ESA, denoted as $\delta^{PD}$. Since $\psi_{0t}{}^D$ is very much improved with $b = b_2 = 0.6$, the corresponding $\delta^{PD}$ turned out to be extremely accurate for all values of the parameter $a$ considered here. The case with $b = b_1 = 0.3$ also improved somewhat. The result is given in Table IV. The one-term distortion potential is then added to this and the phase shifts are calculated, denoted here as $\delta_s{}^D$ in Table VII, and should be compared with $\delta_s$ of Table V. It is reasonable to assume that a three-term diagonalization with $b_1$ and $b_2$, as was done in Sec. III A 1, in addition to $\varphi_0$, should produce very good accuracy in our model.

As stressed in Sec. III A, we have chosen two functions $\varphi_0$ and $\varphi_1$ as our basis set for the entire calculation. Both functions are used to calculate not only the improved target function $\psi_{0t}{}^D$ and $\psi_{1t}{}^D$, but also the $E_{1t}{}^{QD}$ and $\delta_s$, which are closer to what have been expected physically. We have thus shown rather conclusively that the procedure developed here is optimal in so far as the input functions are concerned.

### C. Many-Electron Case

Evidently, in the problems involving more than two electrons, the steps in Secs. III A 1 and III A 3 of the improved procedure are unchanged while the step in Sec. III A 2 requires further clarifications. If $u_n$ of (3.4) are to be determined entirely by solving the coupled scattering equations exactly numerically (or variationally), then no additional requirements are necessary on $u_n$ because they will be *effectively orthogonal*,[15] and the step in Sec. III A 2 is not needed. On the other hand, if the step in Sec. III A 2 is to be carried out, there are two ways of choosing the $v_n$ functions of (3.8′). First, we may pick for $v_n$ one of the single-particle orbitals which is not contained in $\psi_{0t}$, following the general procedure outlined in Ref. 2. There will then be generally some further configuration mixing, the amount of which depends on the choice of the model Hamiltonian used. The second and perhaps more satisfactory way is to solve for the Green's function $G^{Pt} = P_t(E_t - H)P_t{}^{-1}$ and construct a new operator[16] $M_t = H - E_t + (H - E_t)G^{Pt}(H - E_t)$. Noting that $M_t$ is already in the $Q_t$ space, we can effectively replace $(Q_tHQ_t - E_t)$ by $M_t$ in the resonance-state calculation.[16] The procedure to avoid the explicit use of $G^{Pt}$ has been given, and an approximate variational estimate of $G^{Pt}$ may also be useful. Finally, a more satisfactory procedure for the determination of upper bounds on the resonance energies may be given in terms of the minimax theorem, and this will be reported on elsewhere.

TABLE VII. Improved target functions are used to evaluate the static (exchange) shifts and the ones with distortions in the $l = 0$ states. We have $\delta_s{}^D > \delta^{PD}$, as should be, but both $\delta_s{}^D$ and $\delta^{PD}$ have no simple relations to $\delta_s$ and $\delta^P$ of Table IV.

| $b$ | 0.3 | 0.3 | 0.6 |
|---|---|---|---|
| $a$ | $\delta^{PD}(\Delta E_0 = 0)$ | $\delta_s{}^D(\Delta E_0 = 0)$ | $\delta^{PD}(\Delta E_0 = 0)$ |
| 0.7 | 1.369 | 1.378 | 1.236 |
| 0.8 | 1.269 | 1.271 | 1.236 |
| 0.9 | 1.240 | 1.241 | 1.236 |
| 1.0 | 1.237 | 1.241. | 1.237 |

## IV. DISCUSSION

We have seen that the prediagonalization of the cluster energy matrix improves the threshold energies, incorporates the continuum contributions, and gives physically more reasonable values for resonance energies and scattering phase shifts. The method presented in Sec. III is very effective in treating the complex systems without the exact bound-state functions, and optimizes the effect of input functions. It could thus be a basis for the formulation of a simpler theory of the atomic and molecular collisions.

There are several important features of the result for which we have not been able to give rigorous proofs; thus, it is not yet clear whether $E_{nt}{}^{QD}$ always provide bounds on $E_n{}^Q$. We do not know precisely how much $\psi_{0t}$ should be improved before we expect to have bounds on the phase shifts as in the minimum principle, although we have seen some indications for an answer to this problem. In the absence of a more consistent theory, the quantitative study of the model considered here would be helpful in some future applications.

The qualitative conclusions we may draw from the present study are that reliable scattering parameters can be obtained only if the open-channel ($P$) part is treated considerably more accurately than the distortion ($Q$) part, and that the prediagonalization of the cluster energy matrix may be a more consistent approach to many-particle scattering problems.

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## APPENDIX

We consider a bound system described by the Hamiltonian $h$, with the spectrum $E_n$ and assume that some of the low-lying levels are discrete. In order to calculate the energy of the first excited state by the variational principle, either (a) the trial functions $\psi_{nt}$ are to be orthogonalized to the exact ground-state function $\psi_0$ or (b) the Hylleraas-Undheim theorem is applied when the exact $\psi_0$ is not available. These methods then ensure the convergence of $E_{1t}$ to the correct value $E_1$ from above. Obviously, the first approach (a) is a special case of (b) since when one of the $\varphi_{nt}$ is identical to $\psi_0$, say $\varphi_{mt}=\psi_0$, then we immediately have

$$(\varphi_{nt},\, h\varphi_{mt})=\delta_{nm}E_0, \quad \text{where} \quad h\psi_n=E_n\psi_n\ ,$$

as $\varphi_{nt}$, $n\neq m$, can be orthogonalized to $\psi_0$.

We show by a simple argument that, if $\varphi_{nt}$ are orthogonalized to an approximate $\psi_{0t}$, the resulting energy $E_{1t}$ may converge to a value other than $E_0$. $E_{1t}$ may even be close to $E_1$, but, unlike in the HU theorem, the inequality $E_{1t}>E_1$ may not be valid and $E_{1t}$ *depends* both on the accuracy of $\psi_{0t}$ and $\varphi_{nt}$.

The convergence problem can be simply seen by a three-level model. We can then write

$$\varphi_{nt}=a_{n0}\psi_0+a_{n1}\psi_n+a_{n2}\psi_2\ , \tag{A1}$$

with the normalizations

$$a_{n0}{}^2+a_{n1}{}^2+a_{n2}{}^2=1\ , \tag{A2}$$

and where we have

$$(\varphi_{nt}\,,\,\psi_{0t})=0\ .$$

The corresponding energy is given by

$$E_{nt}=a_{n0}{}^2E_0+a_{n1}{}^2E_1+a_{n2}{}^2E_2\ . \tag{A3}$$

Since we have $E_0\leq E_1\leq E_2$, it is clear that, for given $a_{n0}$, $E_{nt}$ will attain the minimum when $a_{n2}=0$. Thus, as more functions are added in a variational calculation, we are essentially making $a_{n2}{}^2=0$ and $a_{n1}{}^2$ minimum for the largest $a_{n0}{}^2$, which is equivalent to a two-level model with one function.

Thus, with $\varphi_t=a_0\psi_0+a_1\psi_1$ and $(\varphi_t,\ \varphi_t)=1$, we have

$$E_t=a_0{}^2(E_0-E_1)+E_1\ , \tag{A4}$$

which implies the following: (i) We have $E_0\leq E_t\leq E_1$ and $E_t$ may converge to a value other than $E_0$ if $a_0\neq 1$, essentially due to the normalization condition. (ii) $E_t$ depends on both $a_0$ and $a_1$, so that the identification $E_t\approx E_1$ is only valid if $a_0$ is reasonably small. (iii) For small $a_0$, $E_t-E_1$ depends also on the size of the gap $E_0-E_1$.

We now apply the same argument to the search for resonance states in our model given in Sec. II. Although the operator $QHQ$ is more involved, the essential convergence property is roughly the same, so that $E_{1t}{}^Q$ calculated with $Q_t\Phi_{nt}$ of (2.12b) could converge to a value lying below the $E_1$ threshold. The above study also indicates that the identification $E_{1t}{}^Q\approx E_1{}^Q$ would be reasonable only if

$$|(E_1{}^Q-E_1)/E_1|\gtrsim|a_0{}^2(E_0-E_1)/E_1|\ .$$

Therefore, if $E_1{}^Q$ is very close to $E_1$ and $a_0{}^2(E_0-E_1)$ is fairly large because either $a_0{}^2$ is large or the gap $(E_0-E_1)$ is large, then the resulting $E_{1t}{}^Q$ will be physically unreliable and thus could be spurious. This is supported by the result of Tables II and III, where $E_{1t}{}^Q$ at $a\neq 1.0$ can be compared with $E_{1t}{}^Q$ at $a=1.0$. Obviously, the actual size of $a_0$ depends strongly on the accuracy of $\psi_{0t}$. (However, as we have seen in Sec. II, the overlap between $\psi_0$

and $\psi_{0t}$ is usually much smaller than the relative error in $\psi_{0t}$.) Therefore, it may not be surprising if $E_{1t}{}^Q$ thus calculated is rather close to its correct value $E_1{}^Q$ for $a_0{}^2$ reasonably small.

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