Adiabatic Approximation and Necessary Conditions for the Existence of Bound States*†‡

F. H. Gertler, H. B. Snodgrass,§ and Larry Spruch
Department of Physics, New York University, Washington Square, New York, New York
(Received 29 January 1968)

Let $H(\vec{\rho},\vec{r})$ represent the $(M-1)$-body Hamiltonian that results from fixing the center of mass $\vec{R}$ of an M-body system, where $\vec{r}$ is the relative coordinate of a particular pair of particles, and $\vec{\rho}$ represents the $M-2$ remaining internal coordinates. With $E_{\rm thr}$ the lowest continuum threshold associated with H, the number of bound states of the system is the number of negative eigenvalues of $H-E_{\rm thr}$. A simple lower bound on H was derived by Hahn and Spruch through the use of an adiabatic-like approximation in which the $(M-1)$-body problem is attacked by considering first an $(M-2)$-body problem and then a one-body problem. With $E_{a0}(r)$ the lowest energy of the system for $\vec{R}$ *and* $\vec{r}$ fixed, one finds

$$H(\vec{\rho},\vec{r})-E_{\rm thr}\geq\hat{1}(\vec{\rho})H^{(1)}(\vec{r}),\quad\text{where } H^{(1)}\equiv T_{\vec{r}}+E_{a0}(r)-E_{\rm thr}\equiv T_{\vec{r}}+V^{(1)}(r).$$

$H^{(1)}$ is a one-body Hamiltonian, $T_{\vec{r}}$ is the kinetic energy operator for the relative motion of the particular pair, and $\hat{1}(\vec{\rho})$ is the unit operator in the space of quadratically integrable functions of $\vec{\rho}$. The adiabatic potential $E_{a0}(r)$ has been tabulated for a number of systems, primarily atomic and molecular. A necessary condition for the existence of a bound state of H is that the lowest eigenvalue of $H^{(1)}$ be negative.

The method is formulated fairly generally and discussed in some detail for the case of Coulomb interactions. It is shown that neither $He+e^+$ nor $\alpha+p+e^-$ can form bound states. We also find lower bounds of -0.068 and -0.065 eV on the energy of the ground state and the first excited state, respectively, of the $H+e^+$ system; presumably there is no bound state of this system, but we are unable to prove it. The system $H+e^-$ is also considered.

I. INTRODUCTION

The number N of bound states of a system of particles is often a matter of great interest in its own right. Because of the intimate connection between bound-state and scattering problems, particularly at zero incident kinetic energy, a knowledge of N can also be very useful in low-energy scattering studies. (Thus, for example, the only available variational upper bound on the scattering length[1,2] demands a precise knowledge of the number N of composite bound states of the target and the incident particle.) When precise knowledge of N is unobtainable, a knowledge of upper and lower bounds on N may still be useful. It is particularly useful to be able to show, when true, that no bound states exist. This requires that one have a *necessary* condition for the existence of bound states.

Sufficient conditions for the existence of N bound states, and therefore lower bounds on the number N, are provided by the Rayleigh-Ritz theorem and its generalization, the Hylleraas-Undheim theorem.[3] However, the determination of upper bounds on N is apparently anything but trivial. Indeed, when looked at from the seemingly most natural point of view, that of the spectrum of the Hamiltonian, it might appear to be impossible. For example, let us restrict ourselves momentarily, for ease of discussion, to a particle of mass m in a spherically symmetric potential $V(r)$ which can support N bound states. Then the spectrum consists, of course, of a continuum running from ∞ down to zero, plus N discrete eigenvalues. If, then, in some approximation scheme we were to obtain such a spectrum (discrete eigenvalues would be somewhat displaced from their true positions), it would seem that, no matter how good the approximation, we would be in some danger of having lost or gained one or more bound states with extraordinarily small binding energy. (Such an approximation might be, for example, the neglect of relativistic effects or finite-mass corrections.) It is, of course, true that a very small perturbation *can* alter the number of bound states, but we will now look at the problem from another viewpoint, one which can show that, as expected, this is highly unlikely.

If $V_-(r)$ is defined as equal to $V(r)$ where $V(r)$ is negative and equal to zero where $V(r)$ is nonnegative, a necessary condition for the existence of a bound state is

$$(2m/\hbar^2)\int_0^\infty r[-V_-(r)]dr\geq 1. \tag{1.1}$$

From this result we may conclude that if, using an approximation which can be expected on physical grounds to be quite good, the numerical value of the left hand side of (1.1) is found to be appreciably less than 1, one would normally have faith that the real system does not have a bound state, not even one with infinitesimal binding. The generalization of (1.1) to necessary conditions for the existence of N bound states merely requires that we increase the numerical value of the right-hand side of (1.1). It is thus apparent that, whereas even a slight change in the potential will make a (slight) change in the discrete energy levels of a system, a more significant change is generally required to move levels into or out of the continuum.

The result embodied in (1.1), and various generalizations, extensions, and improvements all re-

lated to the one-body problem are contained in papers by Jost and Pais,[4] Bargmann,[5] Schwinger,[6] Spruch[7] and Zumino, and Spruch.[8] The strongest result[8] contains a variational trial function, but one must evaluate a much more difficult integral than that in (1.1), since the integrand contains a Green's function. Somewhat different conditions have been given by Friedrichs[9] and by Kato.[10] N can be obtained exactly for the one-body problem by a numerical evaluation of the wave function $\psi(r)$ for the radial zero-energy Schrödinger equation. More generally, as is well known, the number of bound states with energy less than or equal to E is the number of nodes, exclusive of that at $r=0$, of the solution $\psi(r)$ of the radial Schrödinger equation for energy E.

The variational necessary condition referred to above is valid not only for the potential problem but for the many-body problem; the integral is then, of course, even more difficult to evaluate. A second form[8] in which necessary conditions for the many-body problem can be specified is based on the projection operator formalism of Feshbach.[11] This too is quite complicated and has not yet been tested. In this study we will present a less elegant and less general criterion for the many-body problem, but one which reduces, for certain problems, to a form simple enough to be used. Its simplicity arises in part from the possibility of using published "adiabatic potentials."

The basic tool in the present approach is the use of an inequality deduced some years ago by Hahn and Spruch. (It arose in the course of a study of the adiabatic approximation in scattering, in an attempt to obtain the "other" bound on scattering parameters.[12] Though primarily concerned with the scattering problem, Hahn and Spruch recognized at that time, as perhaps many others have before and since, that the adiabatic approximation provides a lower bound on the lowest energy of a system. The question of using that approach in an attempt to prove that bound states of some particular system do not exist, which is the primary purpose of the present paper, did not arise.) The inequality is of the form

$$H-E_{\text{thr}} \geqslant H^{(1)},$$

where H is the full Hamiltonian, E_{thr} is the energy of the deepest continuum threshold of H, and $H^{(1)}$ is a one-body Hamiltonian containing a one-body potential $V^{(1)}$. $H^{(1)}$ does not, unfortunately, contain any variational parameters. $V^{(1)}$ is uniquely defined, formally. For those cases for which $V^{(1)}$ can be found numerically, it is trivial to obtain the lowest eigenvalue $E_0^{(1)}$ of $H^{(1)}$, which always provides a lower bound on the lowest energy eigenvalue of $H-E_{\text{thr}}$. It will often also be possible to obtain improved lower bounds on the first few excited-state energies of $H-E_{\text{thr}}$. It turns out, however, that, if the continua of the spectra of $H^{(1)}$ and $H-E_{\text{thr}}$ do not start at the same value, the present approach cannot be used to prove the nonexistence of bound states; and since the thresholds depend in general on the masses of the interacting particles, severe restrictions are imposed on the problems for which nonexistence can be proved.

A further difficulty that is encountered is that, if $H^{(1)}$ is found to have even one discrete state, no upper limit whatever can be placed on the number of bound states of the original (real) system.

Perhaps the most interesting results obtained are that certain combinations of particles cannot form bound states. These results are not rigorously true since various approximations are made, including the neglect of finite mass and relativistic corrections. As noted above, it is not to be expected, on general grounds, that a rigorous treatment, if possible, would alter the results. One can go even further in the case of relativistic corrections and state that the likelihood of relativistic corrections changing the number of bound states is exceedingly small; for the states in question would be states just bound or just not bound, the velocities (at least for the outer particles) would be very small, and relativistic corrections would be exceedingly small.

II. GENERAL FORMULATION

We consider a nonrelativistic M-body system in which the particles are labeled by the numbers $1, 2, \cdots, M$. We assume central two-body interactions $V_{ij}(r_{ij})$, where $\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$, and we choose as our M independent coordinates the center of mass $\vec{R}$ and $M-1$ relative or internal coordinates. The latter can be chosen in many ways; the only restriction that we will impose is that the set include the coordinate $\vec{r}_{12}$. The remaining $M-2$ coordinates will be denoted collectively by the symbol $\vec{\rho}$. With the center-of-mass motion eliminated, the Hamiltonian will be denoted by $H(\vec{\rho}, \vec{r}_{12})$. Let E_{thr} be defined as the deepest threshold of any continuum in the spectrum of H. (The continua are, of course, associated with distributions of the M particles into two or more separated subsystems.) To prove that the M particles cannot form a bound state, we must show that $H-E_{\text{thr}}$ is a non-negative operator (in the space of quadratically integrable functions).

Separating off the kinetic energy T_{12} of the relative motion of particles 1 and 2, we write

$$H(\vec{\rho}, \vec{r}_{12}) \equiv T_{12}(\vec{r}_{12}) + H_{\text{a}}(\vec{\rho}; \vec{r}_{12}). \tag{2.1}$$

H_{a}, which is defined by the last equation, represents an adiabatic-type Hamiltonian in which $\vec{r}_{12}$ appears only parametrically. We now consider the adiabatic-like eigenvalue problem

$$[H_{\text{a}}(\vec{\rho}; \vec{r}_{12}) - E_{\text{a}n}(r_{12})]\Psi_{\text{a}n}(\vec{\rho}; \vec{r}_{12}) = 0, \tag{2.2}$$

where, for all $\vec{r}_{12}$,

$$\int \Psi_{\text{a}n}^*(\vec{\rho}; \vec{r}_{12})\Psi_{\text{a}m}(\vec{\rho}; \vec{r}_{12})d\vec{\rho} = \delta_{nm}.$$

(This differs from the analogous adiabatic-approximation eigenvalue equation in that we fix $\vec{r}_{12}$ and the center of mass rather than $\vec{r}_1$ and $\vec{r}_2$. The two approximations can become the same if certain of the masses are infinite.) In addition to the continuum, for which the δ_{nm} are Dirac δ functions, H_{a} may or may not have discrete eigenvalues. It is clear from the isotropy of space that the $E_{\text{a}n}$ are functions of r_{12} rather than of $\vec{r}_{12}$. If there is a lowest-energy eigenvalue $E_{\text{a}0}(r_{12})$ for all r_{12}, that

is, if $E_{a0}(r_{12}) \leq E_{an}(r_{12})$ for all n and for all r_{12}, we have

$$H_a(\vec{\rho};\vec{r}_{12}) \geq \hat{1}(\vec{\rho})E_{a0}(r_{12}), \tag{2.3}$$

where $\hat{1}(\vec{\rho})$ is the unit operator in the function space of the internal coordinates $\vec{\rho}$. If there is energy-level crossing at the lowest level, we would merely have to replace $E_{a0}(r_{12})$ by $E_{a\,\min}(r_{12})$, the minimum value of the functions $E_{an}(r_{12})$ for each r_{12}; however, for notational convenience, we will assume that there is no level crossing. It follows then from Eqs. (2.1) and (2.3) that

$$H(\vec{\rho},\vec{r}_{12})-E_{thr} \geq \hat{1}(\vec{\rho})H^{(1)}(\vec{r}_{12}), \tag{2.4}$$

where the one-body Hamiltonian

$$H^{(1)}(\vec{r}_{12}) \equiv T_{12}(\vec{r}_{12}) + V^{(1)}(r_{12}) \tag{2.5}$$

contains the one-body potential

$$V^{(1)}(r_{12}) \equiv E_{a0}(r_{12})-E_{thr}. \tag{2.6}$$

The expectation-value inequality that is the analog of (2.4) can be obtained through the use of the expansion

$$\Psi(\vec{\rho},\vec{r}_{12}) = \sum_n f_n(r_{12})\Psi_{an}(\vec{\rho};\vec{r}_{12}),$$

for Ψ quadratically integrable but otherwise arbitrary. Using this expansion, and Eqs. (2.1) through (2.6), we find

$$J \equiv (\Psi, [H-E_{thr}-T_{12}]\Psi)$$
$$= \sum_{m,n}(f_m\Psi_{am}, [H_a-E_{thr}]f_n\Psi_{an}).$$

We can now replace H_a by E_{an} and then use $E_{an} \geq E_{a0}$, for all r, to arrive at

$$J \geq (\Psi, [E_{a0}-E_{thr}]\Psi) = (\Psi, V^{(1)}\Psi).$$

We now have our analog of (2.4), namely,

$$(\Psi, [H-E_{thr}]\Psi) \geq (\Psi, H^{(1)}\Psi). \tag{2.7}$$

The eigenvalues $E_n^{(1)}$ of the one-body Hamiltonian $H^{(1)}(\vec{r}_{12})$ can readily be obtained numerically, *if* $E_{a0}(r_{12})$ can be determined. By an extension of the minimax theorem, it follows that the $E_n^{(1)}$ provide respective lower bounds of the ordered eigenvalues of $H-E_{thr}$. In particular, $E_0^{(1)}$ provides a lower bound on the lowest eigenvalue of $H-E_{thr}$. Unfortunately, however, because of the appearance of the $\hat{1}(\vec{\rho})$, each eigenvalue of $H^{(1)}(r_{12})\hat{1}(\vec{\rho})$ is infinitely degenerate. The procedure presented thus far, therefore, gives $E_{thr}+E_0^{(1)}$ as the best obtainable lower bound on *all* eigenvalues of H; the procedure does not provide improved lower bounds on the excited states of H. This will be shown to have the unfortunate consequence, in the study of the number of bound states supported by H, that unless we can show that H cannot support any bound states, i.e., that $E_0^{(1)} \geq 0$, we will be unable to show that the number of bound states supported by H is finite. The approach we have outlined can, however, often be modified to provide improved bounds on one or more excited states. Examples will be given later.

The asymptotic value of $V^{(1)}(r)$ is a matter of great interest. A schematic representation of the three possibilities is given in Fig. 1. If $V^{(1)}(\infty) < 0$, then $E_0^{(1)} < 0$, and we cannot hope to prove the nonexistence of an M-body bound state. It is most probably also true that one cannot hope to prove the nonexistence of a bound state if $V^{(1)}(\infty) > 0$. For it follows from the basic inequality (2.4) that, in this case, $H^{(1)}$ must have one or more (infinitely degenerate) *discrete* eigenvalues at or below zero.

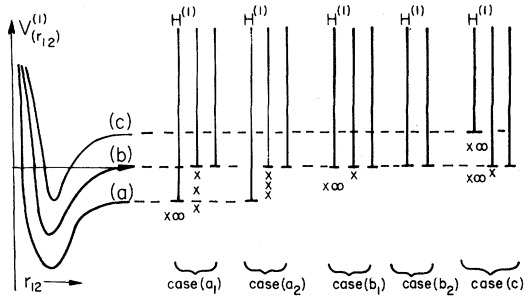

FIG. 1. Schematic representations of the one-body potential $V^{(1)}(r_{12})$, of the spectra of the one-body Hamiltonian $H^{(1)}(\vec{r}_{12})$, and of $H-E_{thr}$, where H is the true Hamiltonian. Nondegenerate and infinitely degenerate eigenvalues are represented by x and x^∞, respectively. For convenience, we assume $V^{(1)}(r_{12})$ to be repulsive for small r_{12}. For each of the five examples of a spectrum of $\hat{1}H^{(1)}$ (the spectrum furthest to the left for each group), we indicate immediately to the right one or two possibilities for the spectrum of $H(\vec{\rho},\vec{r}_{12})-E_{thr}$, where E_{thr} is the deepest continuum threshold of H; the possibilities are limited by the inequality $H-E_{thr} \geq \hat{1}(\vec{\rho})H^{(1)}(\vec{r}_{12})$. The crucial point is whether $V^{(1)}(\infty)$ lies below zero (cases a_1 and a_2), is equal to zero (cases b_1 and b_2), or lies above zero (case c). One is assured of a bound state of $H^{(1)}$ in case c. One can only be certain that H cannot support a bound state if $V^{(1)}(\infty) = 0$ and $H^{(1)}$ cannot support a bound state, i.e., for case b_2.

[The eigenvalues are discrete since they lie below the value $V^{(1)}(\infty)$.] Since they are discrete, one does not expect them to remain stationary under a perturbation, and one therefore expects the lowest eigenvalue of $\hat{1}H^{(1)}$ to lie *below* zero. A more careful analysis would involve a study of the operator

$$H_\lambda(\vec{\rho},\vec{r}_{12}) \equiv (1-\lambda)H(\vec{\rho},\vec{r}_{12}) + \lambda\hat{1}(\vec{\rho})H^{(1)}(\vec{r}_{12})$$

as a function of λ, but we will not pursue the matter for we will never actually use the result that $V^{(1)}(\infty) > 0$ implies that $E_0^{(1)}$ is negative. We do, however, expect that the proof, along the present lines, of the nonexistence of a bound state is possible only if $V^{(1)}(\infty) = 0$. As we shall see, this condition on $V^{(1)}(\infty)$ imposes severe restrictions on the masses of the particles for which one can expect to give such a proof.

III. COULOMB INTERACTIONS—SOME SIMPLE EXAMPLES

The method described in Sec. II can readily be applied to a number of simple systems of charged particles. One can attempt to prove that particular bound states do not exist; if it is known that they

do exist or if one cannot prove that they do not exist, one can obtain a bound on the binding energy. As described in Sec. II, the problem reduces formally to a determination of the lowest eigenvalue associated with an effective one-body Hamiltonian which is known *if* $E_{a0}(r)$, the adiabatic potential, is known. A partial tabulation of the functions $E_{a0}(r)$ to be found in the literature is given in Table I. [Note that we include in our definition of $E_{a0}(r)$ the Coulomb interaction between the two particles that are initially fixed.] The $E_{a0}(r)$ were

TABLE I. Published adiabatic potentials, which are tabulated as functions of the separation of the fixed charges.

System	Fixed charges	Moving particle(s)
$(HeH)^{+}$ [13]	+2, +1	$e^- + e^-$
$(H_2)^{+}$ [15]	+1, +1	e^-
$\mu^- + H$ [16]	+1, −1	e^- (or e^+)
$(HeH)^{++}$ [17]	+2, +1	e^-
H_2 [18]	+1, +1	$e^- + e^-$

obtained in the course of molecular applications of the adiabatic approximation. The masses of the particles that are temporarily "fixed" play no role, and the $E_{a0}(r)$ can therefore also be applied to a number of systems other than those for which the calculations were performed. In Table II we give a summary of the results we will obtain in this section.

The most interesting examples, those for which it may be possible to prove the nonexistence of bound states, are those for which $V^{(1)}(\infty) = 0$. We restrict ourselves in this section to cases for which this condition is satisfied and thereby, as we shall show in Sec. IV, to cases for which one or more of the particles can be taken to have an (effectively) infinite mass.

A. $e^+ + a^{++} + e^- + e^-$

Our first result will be a proof that a positron cannot be bound to a helium atom. We begin by considering a slightly more general system, that of a particle of positive charge e and mass $m^+ \ll M_\alpha$, where M_α is the mass of the α particle, interacting with a helium atom. With the positions of the two positively charged particles fixed, $E_{a0}(r)$ is known from the study of the HeH^+ system.[13] On integrating over that region of r for which $V^{(1)}(r)$ is negative, the integral in (1.1) becomes

$$(2m^+/\hbar^2)\int r[-V_-^{(1)}(r)]dr = 0.421 m^+/m_e,$$

where m_e is the electron mass. It follows immediately that a positron cannot be bound to a helium atom. More generally, a particle of charge $+e$ and mass m^+ such that $m^+ \leq (0.421)^{-1} m_e = 2.38 m_e$ cannot be bound to a helium atom.

The use of Eq. (1.1) is simpler but less accurate than the use of the zero-energy Schrödinger equation for the same $V^{(1)}(r)$. The latter method leads to the better result that there is no bound state for $m^+ \leq 3.25 m_e$.

B. $e^+ + p + e^-$

Since extensive Rayleigh-Ritz calculations have failed to find a positron–hydrogen-atom bound state, it is almost certain that no such bound state exists. (More precisely, a bound state was found, in a Rayleigh-Ritz calculation,[14] only for the positron replaced by a positive charge with a mass $m^+ = 2.625 m_e$.) We are unable to prove the nonexistence of an e^+H bound state but we can obtain a bound on the possible binding energy. (The bound is found to have a very small value.) Furthermore, we can obtain limits on the mass of a particle of charge $+e$ which can be bound to H.

Thus, rather than considering a positron, let us again be more general by considering a particle of positive charge $+e$ and of mass $m^+ \ll M_p$, where M_p is the mass of the proton. We then have $E_{thr} = -m_e e^4/(2\hbar^2)$. The proton will of course be held fixed and either the m^+ or the m_e^- can be held fixed with the other in motion to determine an $E_{a0}(r)$. We will consider each case in turn. Note that in both cases we have $E_{a0}(\infty) = E_{thr}$ and therefore $V^{(1)}(\infty) = 0$.

Holding the m^+ fixed, $E_{a0}(r)$ is the adiabatic potential for the hydrogen molecular ion,[15] and we find

$$(2m^+/\hbar^2)\int r[-V_-^{(1)}(r)]dr = 1.8 m^+/m_e,$$

TABLE II. Summary of results. The superscripts + and − refer to the charge, m represents a light mass, and M a heavy mass. B indicates binding energy, a star refers to the first excited state, and the subscripts s and t refer to singlet and triplet, respectively.

System	Mass values for no composite bound states	Results for physical systems
$M^{++} + m^- + m^- + m^+$	$m^+ \leq 3.25\ m^- \ll M^{++}$	e^+He unbound
$m^- + m^+ + M^+$	$m^+ \leq 0.75\ m^- \ll M^+$	$B(e^+ + H) \leq 0.068$ eV
		$B^*(e^+ + H) \leq 0.065$ eV
$m_1^- + m_2^- + M^+$	$m_2^- \leq 0.66\ m_1^- \ll M^+$	$B_s(e^- + H) \leq 1.85$ eV
		$B_s^*(e^- + H) \leq 0.93$ eV
		$B_t(e^- + H) \leq 0.93$ eV
$M^{++} + (M^+ \text{ or } m^+) + m^-$	$m^- \ll M^{++}$	$\alpha + X^+ + e^-$ unbound, $X^+ = e^+, \mu^+, p^+$, or $d^+ \ldots$

so that a positive charge of mass $m^+ \leq (1.8)^{-1} m_e = 0.56 m_e$ cannot be bound to a hydrogen atom. On using the Schrödinger equation approach with $m^+ = m_e$, we find that the zero-energy wave function has one node (at $\sim 5a_0$). The bound state implied by this node was searched for and found to exist at -0.068 eV. It follows that the binding energy of the $e^+ + H$ bound state, if it exists, is at most 0.068 eV. It was also determined, from the Schrödinger equation, that no bound state exists for $m^+ \leq 0.75\, m_e$. [This represents an improvement, as it had to, on the value $0.56\, m_e$ obtained by the use of Eq. (1.1).] While the result is rigorous, it is probably quite crude. The smallest mass for which a charged particle can be bound to H should be just below the value $2.625\, m_e$ obtained in the calculation[14] quoted above.

A further generalization is easily obtained. It is trivial to show, for three charged particles with masses $M^+ = \infty$, m^+, and m^-, respectively, that the energy scales with the masses for any energy level. If, in particular, there exists a state with energy $E^{(2)}$ in which both m^+ and m^- are bound, we have

$$E^{(2)}(cm^+, cm^-) = cE^{(2)}(m^+, m^-), \tag{3.1}$$

for c a positive constant. [A more general result is given in Eq. (4.8).] We also have for the energy $E_{\rm thr}$ of the hydrogenic $m^- M^+$ bound state

$$E_{\rm thr}(cm^-) = cE_{\rm thr}(m^-). \tag{3.2}$$

Choosing $c = (0.75)^{-1} = 1.33$, $m^+ = 0.75\, m_e{}^+ = 0.75\, m_e$, and $m^- = m_e{}^- = m_e$, it follows that

$$E^{(2)}(m_e{}^+, 1.33 m_e{}^-) - E_{\rm thr}(1.33 m_e{}^-) = 1.33[E^{(2)}(0.75 m_e{}^+, m_e{}^-) - E_{\rm thr}(m_e{}^-)] = 0.$$

In other words, if we increase the mass of the particle of negative charge rather than decrease the mass of the particle of positive charge, we find that a proton, a positron, and a particle of charge $-e$ and mass $\geq 1.33 m_e$ (but still very much smaller than the proton mass) cannot form a three-body bound state.

If we turn now to the second possible approach in which the negatively charged particle with mass m^- is first fixed at coordinate $\vec{r}_2$, with $\vec{r}_1$ assigned to the moving particle m^+, we arrive at

$$H(\vec{r}_1, \vec{r}_2) - E_{\rm thr} \geq \hat{1}(\vec{r}_1)[T_2 + E_{a0}(r_2) - E_{\rm thr}], \tag{3.3}$$

where

$$E_{a0}(r_2) = \mathcal{E}_{a0}(r_2) - e^2/r_2\,. \tag{3.4}$$

$\mathcal{E}_{a0}(r_2)$ is here the energy for the binding of the particle of mass m^+ in the field of a finite dipole, and may be obtained from the finite-dipole data[16] by recognizing that it scales with m^+. [$\mathcal{E}_{a0}(r)$, rather than $E_{a0}(r)$, is generally the function that is tabulated in the literature. A more general scaling law for $\mathcal{E}_{a0}(r)$ is given in (4.9).] Since $\mathcal{E}_{a0}(r_2)$ is here nonpositive and is not identically zero, and since $T_2 - e^2/r_2$ has the eigenvalue $E_{\rm thr}$, it follows that the right-hand side of (3.3) will have a negative eigenvalue. Therefore, if one proceeds by first fixing m^-, it is impossible to prove that m^+ cannot be bound to a proton plus m^-, and in particular not to H, for *any* value of $m^+ (\ll M_p)$.

Departing for the moment from the m^+, m^-, M_p problem, we deduce by an identical argument that one cannot hope to prove the nonexistence of bound states if one first fixes that pair of particles whose ground state determines $E_{\rm thr}$. This negative result represents a limitation of our method. The method cannot, for example, be used to obtain a lower bound on that value Z for which an infinite mass of charge Ze cannot bind two electrons.

In the particular case of e^-, e^+, and p, we could have seen at once, by changing the sign of all the charges and appealing to the experimental fact that H^- is bound, that the approach in which one first fixes the electron could not have proved the nonexistence of a bound state of $m_e{}^+ +$ hydrogen.

We see, then, that the approach in which one first fixes $m_e{}^+$ is superior, which is not surprising for one expects the electron which sees two positive charges to move more rapidly than the positron which sees charges of each sign, and it is more reasonable in the adiabatic approximation to fix the slowly moving particle. It is nevertheless possible to gain some new information by considering this second approach in combination with the first one, for it will lead to an improved bound on the energy of the first *excited* state of $m_e{}^+ +$ hydrogen. It will be recalled that the eigenstate found at the energy 0.068 eV below the hydrogen ground-state level was an infinitely degenerate state. Therefore, the most that follows so far about the first excited state of $m_e{}^+ +$ hydrogen, in the unlikely case that it exists at all, is that it too, as the ground state, is bound by at most 0.068 eV. We will now show how this result can be improved.

The problem of the first excited state can be analyzed in a slightly more general context. Given two particles moving in a center of force and interacting with one another, one can fix either of the particles and thereby obtain the alternative expressions

$$H(\vec{1}, \vec{2}) - E_{\rm thr} \geq H^{(1)}(\vec{1})\hat{1}(\vec{2}) \geq E_0$$

$$H(\vec{1}, \vec{2}) - E_{\rm thr} \geq \hat{1}(\vec{1})H'^{(1)}(\vec{2}) \geq E_0{}',$$

where $\vec{1}$ and $\vec{2}$ represent the coordinates of particles 1 and 2, and $E_0 < 0$ and $E_0{}' < 0$ represent infinitely degenerate states. We take E_0 to lie below $E_0{}'$. For simplicity, we assume that $H^{(1)}(\vec{1})$ and $H'^{(1)}(\vec{2})$ can each support only one bound state. The only conclusion that can as yet be drawn is that any of the (possibly infinite number of) discrete eigenstates of $H(\vec{1}, \vec{2}) - E_{\rm thr}$ lies above E_0. However, for any α such that $0 \leq \alpha \leq 1$, we have

$$\begin{aligned} H(\vec{1}, \vec{2}) - E_{\rm thr} &\geq H_\alpha(\vec{1}, \vec{2}) \\ &\equiv \alpha H^{(1)}(\vec{1})\hat{1}(\vec{2}) + (1-\alpha)\hat{1}(\vec{1})H'^{(1)}(\vec{2}) \\ &\geq \alpha E_0 + (1-\alpha)E_0{}'. \end{aligned} \tag{3.5}$$

$H_\alpha(\vec{1}, \vec{2})$ has a single *nondegenerate* discrete state at $\alpha E_0 + (1-\alpha)E_0{}'$, and continuum thresholds at αE_0, $(1-\alpha)E_0{}'$, and 0. (The continuum associated with the third threshold involves two free particles

as compared to one for the first two cases.) A bound on the first excited state of $H_\alpha(\vec{1},\vec{2})$ and therefore of $H(\vec{1},\vec{2})$ is thus given by the deeper of αE_0 and $(1-\alpha)E_0'$. The best bound, obtained by choosing α such that $\alpha E_0=(1-\alpha)E_0'$, is then $E_0E_0'/(E_0+E_0')$. This is illustrated in Fig. 2. This result can be generalized in many ways. If, for example, $H^{(1)}(\vec{1})$ can support two bound states and $H'^{(1)}(\vec{2})$ can support one, we can obtain a bound on the second excited state which is an improvement upon the bound on the first excited state.

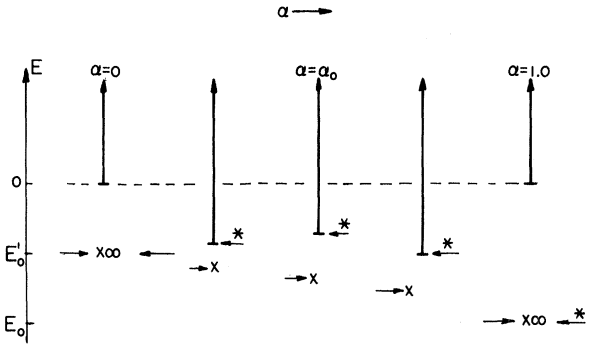

FIG. 2. Improvement of the lower bound on the energy of the first excited state. We have $H(\vec{1},\vec{2})-E_{\rm thr}\geq H_\alpha(\vec{1},\vec{2})$, where $0\leq\alpha\leq 1$ and where H_α is defined by Eq. (3.5). The potentials in both $H^{(1)}$ and $H'^{(1)}$ vanish asymptotically. $H^{(1)}$ and $H'^{(1)}$ each support one bound state, with energies E_0 and E_0', respectively, where $E_0\leq E_0'$. The figure gives the spectrum of $H_\alpha(\vec{1},\vec{2})$ for a number of choices of α. Among them are $\alpha=0$ and 1, for which $H_\alpha(\vec{1},\vec{2})$ reduces to $H^{(1)}(\vec{1})\hat{1}(\vec{2})$ and $\hat{1}(\vec{1})H'^{(1)}(\vec{2})$, respectively; and $\alpha=\alpha_0=E_0'/(E_0+E_0')$, the choice which gives the best possible lower bound, $(E_0E_0')/(E_0+E_0')$, on the energy of the first excited state. The symbols x and x^∞ refer to nondegenerate and infinitely degenerate discrete states, respectively. The symbols $\rightarrow$ and $\stackrel{*}{\leftarrow}$ represent the best lower bounds on the ground-state and first-excited-state energies, respectively, that can be obtained for the given choice of α.

These results can be readily applied to our example of e^+H. Fixing e^+ we obtained the bound $E_0'=-0.068$ eV, while fixing e^- we obtained the bound $E_0=-1.85$ eV. The improved bound on the first excited state is then -0.065 eV. The improvement is so slight because of the disparity of the values E_0 and E_0'.

C. $p+e^-+e^-$

The negative hydrogen ion is known to exist in a singlet state, with the second electron bound by 0.75 eV. There is strong theoretical evidence based on Rayleigh-Ritz calculations that there is not a second bound state. This evidence is strengthened by a consideration of the e^-+hydrogen scattering data.

Let us consider, as usual, a somewhat more general problem, that of a particle with charge $-e$ and mass m^- interacting with a hydrogen atom. Fixing m^- and using the data of Wallis *et al.*[16] we find

$$(2m^-/\hbar^2)\int r[-V^{(1)}(r)]dr=2.5m^-/m_e.$$

It follows that m^- cannot attach itself to hydrogen if $m^-<0.4m_e$. A direct solution of the one-body Schrödinger equation leads to the (necessarily) improved result that there is no such bound state for $m^-\leq 0.66m_e$. Using the scaling argument applied in Sec. III. B, it follows that there is also no such bound state for $m^-\geq(0.66)^{-1}m_e=1.5m_e$, provided again it is still small compared to M_p.

On setting $m^-=m_e^-$, we find that the second electron is bound by at most -1.85 eV. (The number is, of course, the same as that found for e^++hydrogen on fixing the electron; for e^+ or e^- have the same energy $\mathcal{E}_{a0}(r)$ in the fixed e^-p dipole field.) This crude bound is more than twice the true value. Since one can fix either electron, one has, in the notation of Sec. III. B, $E_0=E'_0=1.85$ eV. It follows, on choosing $\alpha=\frac{1}{2}$, that the first excited state is bound by at most $\frac{1}{2}(1.85)$ or 0.93 eV. There is not the slightest evidence for the existence of such a state, and if, by any chance, there is such a state, it must necessarily be bound by less (presumably very much less) than 0.75 eV.

Up to this point we have not used the fact that the electrons are indistinguishable. To do so, we bound $H(\vec{1},\vec{2})$ by a symmetric form

$$H(\vec{1},\vec{2})-E_{\rm thr}\geq\tfrac{1}{2}[H^{(1)}(\vec{1})\hat{1}(\vec{2})+\hat{1}(\vec{1})H^{(1)}(\vec{2})],$$

where $H^{(1)}(i)$ represents the effective one-body Hamiltonian obtained by fixing electron number i. The nondegenerate ground-state energy of the right-hand side, with energy -1.85 eV, is symmetric in the spatial coordinates, while the energy level $-\frac{1}{2}(1.85)$ eV is degenerate, one state being spatially symmetric and the other antisymmetric. We conclude that the singlet ground state is bound by less than 1.85 eV, while both the first excited singlet state and the triplet ground state lie above -0.93 eV.

D. $a+p+e^-$

Consider now an electron, a very heavy particle characterized by M^{++}, and a particle characterized by M^+ or m^+ whose mass can have any value. Fixing M^{++} and M^+(or m^+), the function $E_{a0}(r)$ is provided by the $(HeH)^{++}$ data of Bates and Carson.[17] One immediately finds that $V^{(1)}(r)$ defined in Eq. (1.1) is everywhere repulsive and $V^{(1)}(\infty)=0$. This proves at once that the system $M^{++}+(M^+$ or $m^+)+e^-$ (and, in particular, the system $\alpha+p+e^-$) is not bound. If we replace the electron by a particle characterized by m^-, where $m^-\ll M^{++}$, the new one-body potential, obtained by scaling, is a positive multiple of that obtained for the electron. More generally, then, we find that the system M^{++}, M^+ or m^+, and m^- cannot form a bound state, the only restriction being that $m^-\ll M^{++}$.

IV. COULOMB INTERACTIONS—A MORE GENERAL ANALYSIS

A. Three-Body Problems

In generalizing the treatment of Sec. III, it is con-

venient to introduce some new notation. The only case of interest is that for which two of the particles, to be labeled 1 and 2, have charges q_1 and q_2 of like sign and the third, 3, has a charge q_3 of opposite sign. To simplify the discussion, we set q_1 equal to q_2. The extension to the more general case is trivial. The masses will be denoted by m_1, m_2, and m_3, respectively, where $m_1 \geq m_2$. The two-body ground state for 1 and 3 will then determine $E_{\rm thr}$. We let m_{ij} represent the reduced mass of particles i and j; and i, j, and k represent cyclic permutations of 1, 2, and 3. With the center-of-mass motion separated out, there are three equivalent forms of the Hamiltonian H, one for each choice of the pair of independent orthogonal coordinates $\vec{r}_{ij}(=\vec{r}_i-\vec{r}_j)$ and $\vec{r}_{-k}$, the vector between particle k and the center of mass of particles i and j. (Note the important if obvious fact that $\vec{r}_{-k}$ is a function of m_i and m_j but *not* of m_k.) We introduce the reduced mass m_{-k} defined by

$$m_{-k}^{-1} = m_k^{-1} + (m_i + m_j)^{-1}, \tag{4.1}$$

and the kinetic energy operators

$$T_\gamma = (-\hbar^2/2m_\gamma)\nabla_{\vec{r}_\gamma}^2, \quad \gamma = i,\ j,\ \text{or}\ -k. \tag{4.2}$$

We then have the three possibilities

$$H = T_{ij} + H_{ak} \equiv H_k, \quad k = 1,\ 2,\ \text{or}\ 3, \tag{4.3}$$

where

$$H_{ak} = H_{ak}(\vec{r}_{-k}, \vec{r}_{ij}) = T_{-k} + V_k, \tag{4.4}$$

and where

$$V_k = V_k(\vec{r}_{-k}, \vec{r}_{ij}) = V_{12} + V_{23} + V_{31}$$

represents the sum of the three Coulomb interactions expressed in terms of $\vec{r}_{-k}$ and $\vec{r}_{ij}$. (V_k is therefore a function of m_i and m_j.)

We now introduce the analog of the adiabatic approximation, in which we first fix not $\vec{r}_i$ and $\vec{r}_j$ but rather $\vec{r}_{ij}$ and the center of mass of the system of three particles. With $E_{a0}(r_{ij})$ defined as the lowest eigenvalue of the operator H_{ak} and with $k = 1$, 2, or 3, we have

$$\begin{aligned} H_k - E_{\rm thr} &\geq \hat{1}(\vec{r}_{-k}) H^{(1)}(\vec{r}_{ij}) \\ &\equiv \hat{1}(\vec{r}_{-k})[T_{ij}(\vec{r}_{ij}) + V^{(1)}(r_{ij})], \end{aligned} \tag{4.5}$$

where

$$E_{\rm thr} = -\tfrac{1}{2} m_{13} q_1^2 q_3^2/\hbar^2 \equiv E_{\rm hyd}$$

represents the onset of the lowest continuum associated with the hydrogenic ground state of particles 1 and 3, and where

$$V^{(1)}(r_{ij}) \equiv E_{a0}(r_{ij}) - E_{\rm hyd}. \tag{4.6}$$

The value of $V^{(1)}(r_{ij}=\infty)$ is of immediate interest with regard to the possibility of proving the nonexistence of bound states. As we have noted in Sec. III nonexistence can never be established when we use the formulation indicated by H_2 in which r_{13}, the separation between the two particles which have the deepest two-body bound state, is first held fixed. For the formulation indicated by H_1, we have, dividing by $|E_{\rm hyd}|$ to obtain a dimensionless quantity,

$$\begin{aligned} \frac{V^{(1)}(r_{23}=\infty)}{|E_{\rm hyd}|} &= \frac{m_{13} - m_{-1}}{m_{13}} \\ &= -\frac{m_1 m_2}{m_3(m_1+m_2+m_3)} \leq 0. \end{aligned} \tag{4.7}$$

A rigorous proof of nonexistence, which is not possible for negative $V^{(1)}(r_{23}=\infty)$, therefore demands that $m_2/m_3 = 0$. It is only to the extent that this ratio is vanishingly small that the proofs of Sec. III are valid. When the indices 1 and 3 are interchanged, the discussion for the formulation indicated by H_3 is identical in form to that just given (though the physical situation is quite different). In particular, the relevant ratio is then m_2/m_1.

Though we cannot then in the finite-mass case prove the nonexistence of bound states, we can readily obtain a lower bound on the ground-state binding energy for those values of the masses and charges for which $E_{a0}(r)$ can be determined.

B. Scaling Theorems and Inequalities

It follows quite simply from the Schrödinger equation for a system of M charged particles that if all masses are increased by the same factor α and all charges by the same factor β,

$$E(\{\alpha m_i\}, \{\beta q_i\}) = \alpha\beta^4 E(\{m_i\}, \{q_i\}) \tag{4.8}$$

for any energy eigenvalue in the spectrum. This holds for both discrete states and continuum thresholds, and thus it is also true for an energy measured with respect to a continuum threshold. It follows immediately that the number of bound states (i.e., the number of negative eigenvalues of $H-E_{\rm thr}$) for a system of M charged particles depends on $M-1$ independent mass ratios and $M-1$ independent charge ratios. Equations (3.1) and (3.2) are special cases of (4.8).

It will also be useful to record the scaling law for the ground-state energy $\mathcal{E}_{a0}(r_{ij})$ of a particle of mass m_{-k} and charge q_k moving in the field of charges q_i and q_j, each fixed, at a separation r_{ij}. The energy $\mathcal{E}_{a0}(r_{ij})$ was introduced in a specific case in (3.4), and in general we have

$$\mathcal{E}_{a0}(r_{ij}) = E_{a0}(r_{ij}) - (q_i q_j/r_{ij}). \tag{4.9}$$

One finds from the Schrödinger equation that

$$\begin{aligned} &\mathcal{E}_{a0}(r_{ij}/\alpha\beta\gamma,\ \alpha m_{-k},\ \beta\gamma q_i q_k,\ \beta\gamma q_j q_k) \\ &\quad = \alpha\beta^2\gamma^2 \mathcal{E}_{a0}(r_{ij},\ m_{-k},\ q_i q_k,\ q_j q_k). \end{aligned} \tag{4.10}$$

This relationship enables one to use the published values for the adiabatic potentials to obtain adiabatic potentials for a number of additional cases. It is trivial to give the analog of (4.10) for four or more particles.

It is also of interest to study the behavior of $H_k - E_{\rm thr}$ as a function of the masses. The only simple statement that one can make, apparently, is that $H_2 - E_{\rm thr}$ $(=H-E_{\rm thr})$ increases as m_2 decreases, which is a consequence of the fact that m_2 appears only in the kinetic energy operator. (The

distinctive role played by H_2, as opposed to H_1 and H_3, is a consequence of the m_{13} dependence of $E_{\rm thr}$ and has its origin in the labeling of 1, 2, and 3.)

C. Four-Body Problems

A brief comment on the asymptotic form of $V^{(1)}(r)$ for four-body problems may also be useful. $V^{(1)}(\infty)$ need not now be zero, even when one of the masses can be taken to be infinite. The system $p+e^++e^-+e^-$, with $p+e^+$ fixed, provides a specific example. We here have $E_{\rm thr}=-\frac{3}{2}(e^2/2a_0)$, associated with $(p+e^-)$ and (e^++e^-) existing in isolated systems. As the $p-e^+$ separation goes to infinity, however, we have $E_{a0}(\infty)=-2(e^2/2a_0)$, so that $V^{(1)}(\infty)=-\frac{1}{2}(e^2/2a_0)$. On the other hand, for the $p+e^-+e^-+e^-$ system, $V^{(1)}(r)\to 0$ for $r\to\infty$. This case is of some interest; for it is not inconceivable, owing to the extremely large polarizability of H^-, that an H^{--} system could exist. Unfortunately, however, there exists, to our knowledge, no tabulation of the energy of two electrons in a finite-dipole field.

V. DISCUSSION

The present paper represents some progress in the study of the problem of necessary conditions for the existence of composite bound states, as indicated by the fact that it contains what may be the first proof of the nonexistence of bound states for nontrivial systems, including e^++He and $e^-+\alpha+p$. It can also provide a new lower bound on the energies of the ground state and of one or two low-lying states. The method nevertheless contains a number of weaknesses, some of which have been stated explicitly. As a further indication of its weakness, we note that there exist a number of systems which on physical grounds cannot be expected to be bound, but for which a rigorous proof of nonexistence cannot be found by the present approach. Thus, we showed in Sec. III. A that a system consisting of m^+, m^-, and M^+, in which m^+, $m^-\ll M^+$, and $m^-\geq 1.33m^+$ will not be bound. The restriction $m^-\ll M^+$ does not seem necessary; for as m^- is increased, the particles m^- and M^+ become more tightly bound together and are presumably less affected by the presence of m^+; the electric dipole polarizability of the m^-M^+ system, for example, is proportional to $[1+(M^+/m^-)]^3$. In particular, we therefore expect that the system μ^-+e^++p will not form a bound state, but we cannot prove this. Similarly, we do not expect μ^-+e^-+p to form a bound state, but we cannot prove this.

There is one formal improvement of our results that is trivial to obtain. We restrict ourselves for simplicity to the three-body case with one particle being effectively infinitely massive. As usual, we take the two-body interactions to be central. If there are one or more three-body bound states, the lowest will be a state with zero total angular momentum ($L=0$), a fact not taken into account in our treatment above. Working in the $L=0$ subspace, we have the well-known result

$$H(\vec{1},\vec{2},L=0)-E_{\rm thr}=t(r_1)+t(r_2)+\tfrac{1}{2}\hbar^2(1/m_1r_1^2+1/m_2r_2^2)\mathfrak{L}^2+V-E_{\rm thr},$$

where V is the sum of the three two-body interactions, expressed in terms of r_1, r_2, and $\cos\theta_{12}$, where

$$t(r_i)=-\frac{\hbar^2}{2m_i}\frac{1}{r_i^2}\frac{\partial}{\partial r_i}r_i^2\frac{\partial}{\partial r_i},$$

and where

$$\mathfrak{L}^2=\frac{-1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}}.$$

If we initially fix $\vec{r}_1$, and use the fact that

$$t(r_2)+(\hbar^2/2m_2r_2^2)\mathfrak{L}^2$$

differs from the usual kinetic energy operator T_2 for particle 2 by the term

$$-(\hbar^2/2m_2r_2^2\sin^2\theta_{12})\partial^2/\partial\varphi_2^2,$$

which vanishes for the φ_2 independent ground wave function for particle 2 in the fixed field of the center of force and particle 1, we arrive at

$$H(\vec{1},\vec{2};L=0)-E_{\rm thr}=t(r_1)+H_a(\vec{2};\vec{1};L=0),$$

where

$$H_a(\vec{2};\vec{1};L=0)=H_a(\vec{2};\vec{1})+(\hbar^2/2m_1r_1^2)\mathfrak{L}^2\geq H_a(\vec{2};\vec{1}).$$

It follows that the lowest eigenvalue $E_a(r_1;L=0)$ of $H_a(\vec{2};\vec{1};L=0)$ is greater than or equal to the lowest eigenvalue $E_a(r_1)$ of $H_a(\vec{2};\vec{1})$; that is, we obtain an improved lower bound on $H-E_{\rm thr}$. [The correction term $(\hbar^2/2m_1r_1^2)\mathfrak{L}^2$ will have very little effect if particle 1 is very heavy compared to particle 2—the situation encountered in the molecular cases to which the adiabatic approximation is normally applied.] The difficulty, of course, is that very little has been done in the way of the numerical evaluation of $E_a(r_1;L=0)$.

Were the $E_a(r_1;L=0)$ to be computed for the e^++e^-+p case, it might be possible to prove that e^++H cannot form a bound state. For the e^-H problem, where we necessarily fix two particles which generate $E_{\rm thr}$, the best we can hope for is an improved lower bound; we cannot hope to prove that the triplet state is not bound.

We would like to thank O. Hinckelman for a helpful reading of the manuscript.

*The work reported on in this article was sponsored by the U. S. Office of Naval Research, and the Advanced Research Projects Agency under Contract Nonr-285(49), NRO12-109.

†A preliminary version of this report appears in *Abstracts of the Proceedings of the Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, July* 1967, edited by I. P. Flaks (Nauka, Leningrad, 1967), p. 104.

‡Submitted by F. H. Gertler in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

§Present address: Physics Department and Space Sciences Laboratory, University of California, Berkeley, California.

[1]L. Spruch and L. Rosenberg, Phys. Rev. 116, 1034 1959).

[2]L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. 118, 184 (1960).

[3]E. A. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930).

[4]R. Jost and A. Pais, Phys. Rev. 82, 840 (1951).

[5]V. Bargmann, Proc. Natl. Acad. Sci. U. S. 38, 961 (1952).

[6]J. Schwinger, Proc. Natl. Acad. Sci. U. S. 47, 122 (1961).

[7]L. Spruch, in *Lectures in Theoretical Physics*, edited by W. E. Brittin, J. Downs, and W. B. Downs (Interscience Publishers, Inc., and John Wiley & Sons, Inc., New York, 1962, Vol. IV, p 161 (see especially pp. 196-9) .

[8]L. Spruch, in *Proceedings of the Ninth Summer Meeting of Nuclear Physicists, Hercegnovi*, 1964, edited by M. Cerineo, (Federal Nuclear Energy Commission of Yugoslavia, Belgrade, 1965) , Vol. I, p. 271. This paper also contains a review of earlier work on necessary conditions for the existence of bound states.

[9]K. O. Friedrichs, *Studies and Essays Presented to R. Courant* (Interscience Publishers, Inc., New York, 1948). p. 145.

[10]T. Kato, Math Ann. 162, 258 (1966)

[11]H. Feshbach, Ann. Phys. (N. Y.) 5, 537 (1958); *ibid.* 19, 287 (1962).

[12]Y. Hahn and L. Spruch, Bull. Am. Phys. Soc. 12, 560 (1967), and to be published.

[13]L. Wolniewicz, J. Chem. Phys. 41, 1646 (1964); J. D. Stuart and F. A. Matsen, J. Chem. Phys. 43, 1087 (1965).

[14]A. A. Frost, M. Inokuti, and J. P. Lowe, J. Chem. Phys. 41, 482 (1964).

[15]D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Rcy. Soc. (London) A246, 215 (1954); H. Wind, J. Chem. Phys. 42, 2371 (1965).

[16]A. S. Wightman, Phys. Rev. 77, 521 (1950); R. F. Wallis, R. Herman, and H. W. Milnes, J. Mol. Spectry. 4, 51 (1960).

[17]D. R. Bates and T. R. Carson, Proc. Roy. Soc. (London) A234, 207 (1956).

[18]W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).

Resonance Scattering and the Drift Motion of Electrons through Gases*

Lothar Frommhold
Physics Department and Electronics Research Center, University of Texas, Austin, Texas
(Received 16 February 1968; revised manuscript received 29 March 1968)

Density-dependent values of the electron drift velocity in hydrogen, deuterium, and nitrogen gas have recently been reported. Their reciprocal values are shown to be a linear function of the gas density. Several possible theoretical explanations are discussed, some of which lead to such a linear pressure dependence. It is concluded that electron trapping by some low-energy resonance states is likely to take place. "Rotational resonances" in atom-rotator scattering have been described in a theoretical paper by Kouri, and it is thought that rotational resonances should be observed in electron-molecule scattering as well, at electron energies close to thermal energy. At the higher electron energies ($\simeq$1 eV), the known "single-particle" resonance states of H_2 and N_2 near 2 eV are probably responsible for the delay in the electron motion at high densities.

INTRODUCTION

According to the well-known theories of the drift motion of electrons through gases,[1,2] the electron drift velocity v_e should be a function of the ratio of electric field to pressure, E/p, of the gas temperature T, and of the nature of the gas, but not of its density. Recently, however, in very accurate measurements of the electron drift velocity in gases, a dependence upon the neutral density was found. Lowke[3] was able to show that in nitrogen, at low temperatures and varying densities up to 7×10^{19} cm^{-3}, electron drift velocities decrease slightly (by 3%) with increasing densities. Grünberg[4] found similarly, at room temperatures and at higher densities in hydrogen and nitrogen, drift velocities decreasing with increasing densities. Variations of v_e in hydrogen of up to 30% for neutral densities up to 10^{21} cm^{-3} have been reported in this experiment.[4] In deuterium gas at 77°K, density-dependent drift velocities of electrons have also been reported.[5]

The reason for the observed density dependences is not clear, although the fact that such a dependence exists is not really surprising. Several possible reasons have been mentioned in the past and will be reviewed here, after the experimental evidence is presented in a new form.

Since several theoretical considerations to be discussed suggest that the inverse drift velocity