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Theory of the Quenching of Metastable Hydrogen Atoms by Helium

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In this article we analyze the quenching of metastable hydrogen atoms by helium in the energy range below roughly 250 eV. Two methods are discussed. In one, a perturbation-theory approach is used; in the other, a pseudopotential is employed which attempts to relate the quenching matrix elements to low-energy-electron elastic scattering data. At thermal energies, both methods predict very large quenching cross sections. The pseudopotential approach gives a result of about $80\pi a_0^2$, while the perturbation analysis yields $40\pi a_0^2$. As one goes to higher energies, the cross sections decrease, with the pseudopotential result falling off much less rapidly than the perturbation-theory result. Reasonable agreement between experiment and the pseudopotential method is found at about 300 eV, which is the lowest energy experimentally available at present.

I. INTRODUCTION

The study of the quenching of metastable hydrogen by its interaction with various systems has proven to be of considerable theoretical and experimental interest. This has been due both to the theoretical simplicity of the hydrogen atom and the advanced technology associated with the production of metastable hydrogen beams. Research in this program is currently directed towards the investigation of collisions between metastable hydrogen atoms and simple atoms and molecules.

The mechanism responsible for the quenching may be understood simply as follows. In the absence of external perturbations, the hydrogen $2s$ state would decay primarily by two-photon emission to the ground state, with a lifetime of approximately $\frac{1}{7}$ sec. In the presence of time-dependent perturbations, however, transitions to the $2p$ state are induced and subsequent radiative deexcitation will ensue. The quenching of metastable hydrogen atoms by static electric fields[1] and by ions[2] has been discussed previously. In an experiment designed to determine the $2s$-state lifetime, cross sections for the quenching caused by molecules were measured.[3] Quenching cross sections for hydrogen-molecule targets have also been reported.[4] The theory for the quenching caused by molecules at low energies has been given.[5] There the quenching was found to be caused by the electric fields which stem from the molecular multipole moments.

More recently, experimental effort has gone into measuring the cross sections for quenching by atoms.[6] In the present paper we develop a theory for such processes. We begin by analyzing the dynamics of the problem focusing our attention on the low-velocity region where only transitions between the metastable state and the nearby $2p$ state are important. After reformulating the problem in terms of certain effective one-body potentials, we consider the problem of evaluating these potentials in an approximate manner. We use two methods. The first is based on perturbation theory. This necessitates the development of an exact method for obtaining the effective potentials at large internuclear separations. The exact asymptotic potentials are used to normalize certain of our perturbation-theory results. Next we utilize a semiphenomenological method to obtain the effective potentials. This method replaces the helium atom by a Breit-Fermi pseudopotential whose magnitude is determined from scattering lengths found in electron-helium scattering experiments. Finally, with the relevent potentials having been determined by two independent methods, we obtain results for the quenching of metastable hydrogen by helium which can be compared with experiment.

II. THEORETICAL PRELIMINARIES

At the energies of interest in this paper, the problem may be viewed as that of a heavy projectile following a classical straight-line path which impinges on a target, producing excitation of the projectile or the target. Because of the slowness of the projectile ($v \ll 1$, in a.u., which we will use throughout this work), only states very close in energy to the initial state can be excited with appreciable probability. Thus, if both the target atom and the projectile were in their respective ground states, we should have only elastic scattering (unless there is a pseudocrossing of atomic levels as a function of internuclear separation). However, when the incident hydrogen atom is in its metastable $2s$ state, transitions to the nearby (essentially degenerate) $2p$ state can occur with high probability.

We must therefore attempt to solve Schrödinger's equation in the form

$$i\frac{d\Psi^{(2s)}}{dt}=[H_0+V(t)]\,\Psi^{(2s)}\ , \tag{1}$$

where $\Psi^{(2s)}$ is a solution which at remote past times represents a hydrogen atom in its $2s$ state and a target atom in its ground state. $V(t)$ is the interatomic potential which depends on t via the internuclear distance, which may be written as

$$R=(b^2+v^2t^2)^{1/2}, \tag{2}$$

b being the impact parameter and v the relative velocity of the collision. We will take the incident velocity to lie along the z axis. We wish to find $\Psi^{(2s)}$ at remote future times; the component of $\Psi^{(2s)}(t=+\infty)$ along the state vector corresponding to a target atom in its ground state and a hydrogen atom in its $2p$ state will give us the probability of a transition to the $2p$ state.

Suppose that $\{\psi_n(t)\}$ is the complete set of orthonormal solutions to

$$[H_0+V(t)]\psi_n(t)=E_n(t)\,\psi_n(t)\ . \tag{3}$$

[We are displaying only the t dependence; of course $\psi_n(t)$ and $V(t)$ depend also on impact parameter as well as on all the internal coordinates of the target and the projectile.] Let us assume for the moment that we know $E_n(t)$ and $\psi_n(t)$ for all n. Writing

$$\Psi^{(2s)}(t)=\textstyle\sum_n a_n^{(2s)}(t)\,\psi_n(t)\ , \tag{4}$$

we obtain from Eqs. (1) and (3)

$$\dot{a}_n^{(2s)}(t)+\sum_{n'}\big(\psi_n(t),\ \dot{\psi}_{n'}(t)\big)a_{n'}^{(2s)}(t)=-i\,E_n(t)\,a_n^{(2s)}(t)\ . \tag{5}$$

The boundary condition is

$$a_n^{(2s)}(t=-\infty)=\delta_{2s,n}\ . \tag{6}$$

To appreciate the important magnitudes, it is convenient to change from the variable t to $Z=vt$. Then Eqs. (5) and (6) become

$$\frac{da_n^{(2s)}(Z)}{dZ}+\sum_{n'}\left(\psi_n,\frac{d\psi_{n'}}{dZ}\right)a_{n'}^{(2s)}(Z)=-\frac{i}{v}\,E_n(Z)\,a_n^{(2s)}(Z)\ , \tag{7}$$

$$a_n^{(2s)}(Z=-\infty)=\delta_{2s,n}\ . \tag{8}$$

As is well known, the only states of any importance are those for which

$$|\,E_{2s}(\vec{\mathrm{R}})-E_n(\vec{\mathrm{R}})\,|/v\ll 1$$

over a significant range of internuclear separations. In our case, it is clear that the $2p$ state of hydrogen will very likely stay close to the $2s$ state as a function of internuclear distance from very large separations down to fairly small separations. This is in contradistinction to the more familiar "level crossing" case, where two levels, which are asymptotically separated by a large amount, can come very close together over some small region of internuclear distances.

Thus, in summary, our problem comes down to solving

$$\frac{da_n^{(2s)}(Z)}{dZ}+\sum_{n'\in I}\left(\psi_n,\frac{d\psi_{n'}}{dZ}\right)a_{n'}^{(2s)}(Z)=-\frac{i}{v}\,E_n(Z)a_n^{(2s)}(Z) \tag{9}$$

for all $n\in I$ subject to

$$a_n^{(2s)}(Z=-\infty)=\delta_{2s,n}\ . \tag{10}$$

In Eq. (9) we have used the symbol I to denote the index set consisting of the four states $(2s, g)$, $(2p_+, g)$, $(2p_0, g)$, and $(2p_-, g)$, where g denotes the ground state of the target atom.

It is now necessary to discuss $E_n(Z)$ and $\psi_n(Z)$ in some detail. Since the $2s$ and $2p$ states are asymptotically degenerate, we must consider them together and obtain ψ_n and E_n by degenerate perturbation theory. Let us denote the zero-order wave functions of the system by ϕ_n and their corresponding eigenvalues by ϵ_n. Then, to second order in the potential, the interaction matrix is

$$M_{jj'}=(\phi_j,\ V\phi_{j'})+\sum_{m\notin I}\frac{(\phi_j,\ V\phi_m)(\phi_m,\ V\phi_{j'})}{\epsilon-\epsilon_m}\ . \tag{11}$$

Let U be the matrix which diagonalizes M. Thus

$$U^{-1}MU=D\ , \tag{12}$$

where D is a matrix whose diagonal elements are the E_n. Then Eq. (5) becomes

$$\frac{da_n^{(2s)}}{dZ}+\sum_{k\in I}\ \sum_{n'\in I}U_{kn}^{*}\frac{dU_{kn'}}{dZ}\,a_{n'}^{(2s)}=-\frac{i}{v}\,E_n a_n^{(2s)}\ . \tag{13}$$

Letting $a^{(2s)}$ denote the column vector whose elements are the $a_n^{(2s)}$ and recalling that the U_{mn} form a unitary matrix, we have in matrix notation

$$\frac{da^{(2s)}}{dZ}+U^{-1}\frac{dU}{dZ}\,a^{(2s)}=-\frac{i}{v}\,Da^{(2s)}\ , \tag{14}$$

where D is the diagonal matrix defined above. Making the definition $\alpha^{(2s)}\equiv Ua^{(2s)}$ and using Eq. (12), we may rewrite Eq. (14) in the simple form

$$\frac{d\alpha^{(2s)}}{dZ}=-\frac{i}{v}\,M\alpha^{(2s)}\ , \tag{15a}$$

where M is defined in Eq. (13). Since the matrix U tends to the unit matrix for large internuclear distances, we have

$$\alpha_n^{(2s)}(b,\ Z=\pm\infty)=a_n^{(2s)}(b,\ Z=\pm\infty)\ ,$$

and thus the same boundary conditions apply to the equation for $\alpha^{(2s)}$ as to the equation for $a^{(2s)}$. Also the quantity $|\alpha_n^{(2s)}(b,\ Z=+\infty)|^2$ gives the probability, as a function of impact parameter, for finding the system in the state n after a collision. Equation (15a) can be written in component form as

$$\frac{d\alpha_n^{(2s)}}{dZ}=-\frac{i}{v}\sum_{n'\in I} M_{nn'}\,\alpha_{n'}^{(2s)}\ , \tag{15b}$$

subject to the boundary condition $\alpha_n^{(2s)}(b,\ Z=-\infty)$ $=\delta_{2s,n'}$.

This is a system of four coupled differential equations. The key ingredient in their solution will be the determination of the matrix M, whose elements are given by the formidable Eq. (11). It is to this problem that we now turn our attention.

III. COMPUTATION OF INTERATOMIC POTENTIALS

The problem to be considered in this section is that of evaluating the elements of the 4×4 matrix

$$M_{jj'}=(\phi_j,\ V\phi_{j'})+\sum_{m\notin I}\frac{(\phi_j,\ V\phi_m)(\phi_m,\ V\phi_{j'})}{\epsilon-\epsilon_m}\ , \tag{16}$$

where $j,\ j'\in I$. The sum in Eq. (16) is far too complicated to be evaluated for any but the simplest of systems, except in certain limiting conditions. In this section we confine our attentions to the case when the target gas is helium. The problem of more general target gases will be discussed in a limited context in Sec. IV.

For the purpose of evaluating the integrals implied by the matrix elements in Eq. (16) we can write V in the form

$$V=\frac{2}{R}-\frac{1}{|\vec{R}+\vec{r}_1'|}-\frac{1}{|\vec{R}+\vec{r}_1'|}-\left[\frac{2}{|\vec{R}-\vec{r}_2|}\right.$$
$$\left.-\frac{1}{|\vec{R}+\vec{r}_1-\vec{r}_2|}-\frac{1}{|\vec{R}+\vec{r}_1'-\vec{r}_2|}\right]. \tag{17}$$

Here $\vec{R}$ is the vector from the hydrogen nucleus to the helium nucleus, $\vec{r}_1$ and $\vec{r}_1'$ are the vectors from the helium nucleus to the two helium electrons, and $\vec{r}_2$ is the coordinate of the hydrogen electron. In this coordinate system, a typical ϕ_j would look like

$$\phi_{2s,g}=\chi_g(\vec{r}_1,\ \vec{r}_1')\,\omega_{2s}(\vec{r}_2)\ .$$

In what follows, we will use the simplest screened hydrogenic wave function with $Z^*=\frac{27}{16}$ for the helium ground state:

$$\chi_g(\vec{r}_1,\ \vec{r}_1')=(Z^{*3}/\pi)\,e^{-Z^*(r_1+r'_1)}\ .$$

The first term in Eq. (13) is readily evaluated using the simple properties of our χ_g. Doing the helium integrals and using an obvious notation which surpresses the implied ground-state configuration of helium, we have

$$(\phi_j,\ V\phi_{j'})=(\omega_j,\ \tilde{V}\omega_{j'})\ , \tag{18}$$

where

$$\tilde{V}(\vec{R},\ \vec{r}_2)=2(Z^*+1/R)\,e^{-2Z^*R}$$
$$-2(Z^*+1/|\vec{R}-\vec{r}_2|)\,e^{-2Z^*|\vec{R}-\vec{r}_2|}\ . \tag{19}$$

Note that the first term in Eq. (19) contributes only to diagonal matrix elements, and its contribution to each diagonal element is the same. It therefore cannot contribute to any inelastic process, so we will neglect it in what follows. Thus,

$$(\phi_j,\ V\phi_{j'})=-2\int\omega_j^*(r_2)\,[Z^*$$
$$+1/|\vec{R}-\vec{r}_2|\,]\,e^{-2Z^*|\vec{R}-\vec{r}_2|}\,\omega_{j'}(\vec{r}_2)\ . \tag{20}$$

When j or j' is equal to $2s$, $2p_+$, $2p_0$, or $2p_{-1}$ this expression may be readily evaluated. By symmetry, it is clear that there are only four nontrivial quantities of interest. Elementary angular momentum considerations enable us to write

$$(\phi_{2pm'},\ V\phi_{2pm})=\delta_{m'm}f_0(R)+A_{m'm}f_2(R)$$
$$\times\left[\sqrt{\tfrac{4}{5}\pi}\ Y_{2,m-m'}(\theta,\ \phi)\right]\ , \tag{21a}$$

$$(\phi_{2s},\ V\phi_{2pm})=g(R)\left[\sqrt{\tfrac{4}{3}\pi}\ Y_{1,m}(\theta,\ \phi)\right]\ , \tag{21b}$$

$$(\phi_{2s},\ V\phi_{2s})=h(R)\ , \tag{21c}$$

where $A_{m'm}$ is given by

$$A_{m'm}=\begin{pmatrix}-1 & -\sqrt{3} & -\sqrt{6}\\ \sqrt{3} & 2 & \sqrt{3}\\ -\sqrt{6} & -\sqrt{3} & -1\end{pmatrix}. \tag{22}$$

The variables θ and ϕ define the orientation of the internuclear distance $\vec{R}$. Note that although $A_{m'm}$ is not Hermitian, $A_{m'm}Y_{2,m-m'}$ is Hermitian. It is possible to obtain exact expressions for f_0, f_2, g, and h, but they are very cumbersome. We omit these results and show in Fig. 1 a graph of the four quantities of interest.

If we treat the potential in the integral of Eq. (20) as a δ function in the variable $\vec{R}-\vec{r}_2$, we can obtain approximate expressions for f_0, f_2, g, and h which are quite accurate down to about $R=2$. We have

$$(\phi_j,\ V\phi_{j'})=-2\omega_j^*(\vec{R})\,\omega_{j'}(\vec{R})\int[Z^*+1/|\vec{R}-\vec{r}_2|\,]$$
$$\times e^{-2Z^*|R-r_2|}\,d\vec{r}_2\ .$$

The integral is elementary to evaluate, so we find

$$(\phi_j,\ V\phi_{j'})=-(4\pi/Z^{*2})\,\omega_j^*(\vec{R})\,\omega_{j'}(\vec{R})\ .$$

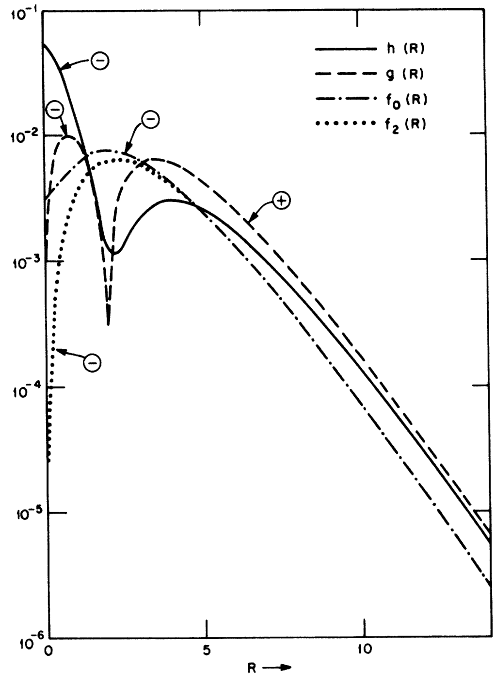

FIG. 1. First -order contributions to the $2s$-$2s$, $2s$-$2p$, and $2p$-$2p$ matrix elements. The sign of the matrix elements is given explicitly. Notice that $g(R)$ changes sign at $R=2$, and that the $2p$-$2p$ element has an $L=0$ part and an $L=2$ part, which are shown separately.

Thus, we have

$$f_0(R)\simeq f_2(R)\simeq -(1/24Z^{*2})R^2e^{-R} , \tag{23a}$$

$$g(R)\simeq -(1/4Z^{*2})(1-\tfrac{1}{2}R)Re^{-R} , \tag{23b}$$

$$h(R)\simeq -(1/2Z^{*2})(1-\tfrac{1}{2}R)^2e^{-R} . \tag{23c}$$

The second term in Eq. (16) is not trivial to evaluate. It is also clear that it cannot be neglected, for at large distances it will fall off like some inverse power of R (the power depending on ϕ_j and $\phi_{j'}$), whereas $(\phi_j,\ V\phi_{j'})$ falls off exponentially for all j and j' with helium in its ground state. Let us write this term as a sum of two terms:

$$M_{jj'}=(\phi_j,\ V\phi_{j'})+M^e_{jj'}+M^g_{jj'} , \tag{24}$$

where

$$M^g_{jj'}=\sum_{m\notin I}{}' \frac{(\phi_j,\ V\phi_m)(\phi_m,\ V\phi_{j'})}{\epsilon-\epsilon_m} , \tag{25a}$$

$$M^e_{jj'}=\sum_{m}{}'' \frac{(\phi_j,\ V\phi_m)(\phi_m,\ V\phi_{j'})}{\epsilon-\epsilon_m} . \tag{25b}$$

In the first sum, the prime indicates that the sum runs over only intermediate states in which the helium target remains in its ground state. This term will fall off exponentially at large distances. Using Eqs. (18)–(20), Eq. (25a) can be rewritten as

$$M^g_{jj'}=\sum_{m\notin I} \frac{(\omega_j,\ \tilde{V}\omega_m)(\omega_m,\ \tilde{V}\omega_{j'})}{\epsilon-\epsilon_m} . \tag{26}$$

It is fairly straightforward to evaluate this sum by variational methods.

The expression in Eq. (25b) is much more complicated. In this equation the double prime on the summation indicates that we include only excited helium configurations as intermediate states. In general, one cannot obtain an exact value for this term, but fortunately at asymptotically large internuclear separations an exact result can be found. In Sec. IV. we will obtain such results, not only for a helium target, but for all noble gases. At nonasymptotic distances, we try the following procedure. The denominator is replaced by an average demoninator Δ so that the sum may be evaluated by closure. Doing this, we obtain

$$M^e_{jj'}=(1/\Delta)\left[(\phi_j,\ V^2\phi_{j'})-(\omega_j,\ \tilde{V}^2\omega_{j'})\right] . \tag{27}$$

Using the results of Sec. IV., which give $M^e_{jj'}$ exactly at large separations, we can fix Δ. In doing this we are assuming the R dependence of Δ to be unimportant.

Equation (27) cannot be evaluated in closed form, but it can be simplified by Fourier transforming everything and working in momentum space. It is then possible to reduce the nine-dimensional integrals implied by Eq. (27) to a one-dimensional integral which can be done numerically. As in the case of $(\phi_j,\ V\phi_{j'})$ the results can be written as

$$M^e_{2pm',2pm}=\delta_{m'm}F^e_0(R)$$
$$+A_{m'm}F^e_2(R)\left[\sqrt{\tfrac{4}{5}\pi}\,Y_{2,m-m'}(\theta,\ \phi)\right] , \tag{28a}$$

$$M^e_{2s,2pm}=G^e(R)\left[\sqrt{\tfrac{4}{3}\pi}\,Y_{1,m}(\theta,\ \phi)\right] , \tag{28b}$$

$$M^e_{2s,2s}=H^e(R) . \tag{28c}$$

$A_{m'm}$ is given by Eq. (22). Since the expressions for F^0_e, F^e_2, G^e, and H^e are uninstructive and very lengthy, we will not reproduce them here but will show them in Fig. 2. We have used the value $\Delta=-1.09$, obtained from Sec. IV. Note that the four functions shown in Fig. 2 are significantly larger than the "first-order" functions of Fig. 1.

It is possible to extract from Eq. (27) the asymptotic behavior of F^e_0, F^e_2, G^e, and H^e by expanding the potentials in multipoles. One finds, for example,

$$H^e(R)\simeq \frac{1}{\Delta}\left[\frac{59}{R^6}+\frac{6100}{R^8}+\cdots\right] , \tag{29a}$$

$$G^e(R)\simeq -\frac{1}{\Delta}\left[\frac{755}{R^7}+\frac{88\,300}{R^9}+\cdots\right] . \tag{29b}$$

Similar expressions may be obtained for F^e_0 and F^e_2. The most striking feature of these equations

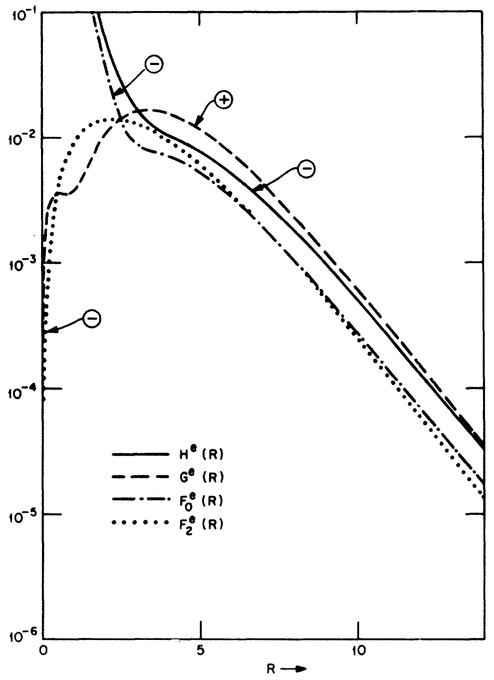

FIG. 2. Long-range part of the second-order contributions to the matrix elements.

is the fact that they show that at $R = 10$ one is still a long way from the asymptotic region. In fact, it is not until about $R = 20$ that the form of the matrix elements begins to look asymptotic.

It is interesting to compare these results with analogous ones obtained by a semiempirical method.[7] We could consider the target to be simply a polarizable atom, taking the polarizability to be given by experiment. Then in the electric field of the hydrogen atom, we find an additional potential energy given by

$$U = -\tfrac{1}{2}\alpha E^2 = -\tfrac{1}{2}\alpha\left[\frac{\hat{R}}{R^2} - \frac{1}{|\vec{R}-\vec{r}_2|^2}\,\frac{\vec{R}-\vec{r}_2}{|\vec{R}-\vec{r}_2|}\right]^2 . \tag{30}$$

The matrix elements of interest to us will be $(\omega_j,\ U\omega_{j'})$. These matrix elements will diverge because of the form of U, so let us cut the potential off by writing empirically

$$U = -\tfrac{1}{2}\alpha\left[\frac{\hat{R}}{R^2+a^2} - \frac{1}{|\vec{R}-\vec{r}^2|^2+a^2}\,\frac{\vec{R}-\vec{r}_2}{|\vec{R}-\vec{r}_2|}\right]^2 . \tag{30$'$}$$

This cuts off U in a plausible way as we get inside the target atom. For helium, we would expect a to have a value like $1/Z^*$ ($\cong 0.6$), corresponding to the maximum point of the helium ground-state charge density. Using this value for a and the experimental value $\alpha = 1.38$ one obtains values for F_0^e, F_2^e, G^e, and H^e which agree for $R \gtrsim 4$ to within 20% with the results shown in Fig. 2. Asymptotically, for example, one finds

$$(\omega_{2s},\ U\omega_{2s}) \cong -42\alpha/R^6 = -58/R^6 .$$

This is to be compared with the leading term in Eq. (29a) which gives

$$H^e(R) \cong -54/R^6 \tag{31a}$$

for $\Delta = -1.09$. Similarly, one finds

$$(\omega_{2s},\ U\omega_{2pm}) = (540\alpha/R^7)\left[\sqrt{\tfrac{4}{3}\pi}\ Y_{1,m}(\theta,\ \phi)\right]$$
$$= (745/R^7)\left[\sqrt{\tfrac{4}{3}\pi}\ Y_{1,m}(\theta,\ \phi)\right] .$$

The coefficient of the term in brackets is to be compared with Eq. (29b), which gives

$$G^e(R) \cong 686/R^7 \tag{31b}$$

for $\Delta = -1.09$. Thus, our average energy denominator method seems to check well with the empirical approach, although it should be pointed out that in the region of most physical interest, namely, $R \lesssim 10$, the magnitude of the matrix elements of U depends rather seriously on the choice of a, even though the asymptotic expansion is unaffected by this choice.

It remains only to discuss the modifications of the second-order potential which comes from Eq. (26). The sum given in that equation could, of course, be evaluated by the same closure methods used on $M^e_{jj'}$, but in this case we have no asymptotic technique available for determining the average energy denominator. Instead let us proceed as follows. We define

$$W(\vec{\rho}) = -2(Z^* + 1/\rho)\,e^{-2Z^*\rho} ; \tag{32}$$

then if we can solve

$$\left(-\tfrac{1}{2}\nabla^2 - 1/r + \tfrac{1}{8}\right)\psi_j(\vec{r}) = -W(\vec{R}-\vec{r})\,\omega_j(\vec{r}) \tag{33}$$

for $j = 2s$, $2pm$ subject to the constraint that ϕ_j contain no components of ω_{2s} or ω_{2pm}, we have simply

$$M^g_{2s,2s} = (\omega_{2s},\ W(\vec{R}-\vec{r})\,\psi_{2s}) , \tag{34a}$$

$$M^g_{2s,2pm} = (\omega_{2s},\ W(\vec{R}-\vec{r})\,\psi_{2pm}) , \tag{34b}$$

$$M^g_{2pm',2pm} = (\omega_{2pm'},\ W(\vec{R}-\vec{r})\,\psi_{2pm}) . \tag{34c}$$

We proceed by introducing the Coulomb Green's function $G(\vec{r},\ \vec{r}\,')$ which satisfies

$$\left(-\tfrac{1}{2}\nabla^2 - 1/r + \tfrac{1}{8}\right)G(\vec{r},\ \vec{r}\,') = -\delta(\vec{r}-\vec{r}\,') . \tag{35}$$

Since the energy appearing on the left-hand side is an eigenvalue, G will be finite only if it does not include $2s$ or $2pm$ contributions. In terms of this restricted Green's function we may rewrite Eq. (34) as

$$M^g_{jk} = \iint \omega_j(\vec{r})\,W(\vec{r}-\vec{R})\,G(\vec{r},\ \vec{r}\,')\,W(\vec{r}\,'-\vec{R}) \times \omega_k(\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' . \tag{36}$$

Integrating Eq. (35) around a small sphere in the neighborhood of $\vec{r}=\vec{r}\,'$ it is easy to show that $G(\vec{r}, \vec{r}\,')$ can be written in the form

$$G(\vec{r}, \vec{r}\,')=-\frac{1}{2\pi}\frac{F(\vec{r}, \vec{r}\,')}{|\vec{r}-\vec{r}\,'|} .$$

The function F is smoothly varying and $F(\vec{R}, \vec{R})=1$. The function $W(\vec{\rho})$ is sharply peaked about $\vec{\rho}=0$ and so, to a good approximation, we have

$$M^{g}_{jk}=-\frac{1}{2\pi}\,\omega_j(\vec{R})\omega_k(\vec{R})\int\!\!\int\frac{W(\vec{\rho})W(\vec{\rho}\,')}{|\vec{\rho}-\vec{\rho}|}\,dp\,dp\,' .$$

Upon expanding the denominator in terms of Legendre polynomials this expression reduces to a sum of elementary integrals. Thus we find

$$M^{g}_{jk}=-(25\pi/4Z^{*3})\,\omega_j(\vec{R})\omega_k(\vec{R}) . \qquad (37)$$

Thus we have

$$M^{g}_{2pm',2pm}=\delta_{m'm}F^{g}_{0}(R)+A_{m'm}F^{g}_{2}(R)$$

$$\times\left[\sqrt{\tfrac{4}{5}\pi}\;Y_{2,m-m'}(\theta, \phi)\right] , \qquad (38a)$$

$$M^{g}_{2s,2pm}=G^{g}(R)\left[\sqrt{\tfrac{4}{3}\pi}\;Y_{1,m}(\theta, \phi)\right] , \qquad (38b)$$

$$M^{g}_{2s,2s}=H^{g}(R) , \qquad (38c)$$

with

$$F^{g}_{0}(R)=F^{g}_{2}(R)=(-25/384Z^{*3})R^2e^{-R} , \qquad (39a)$$

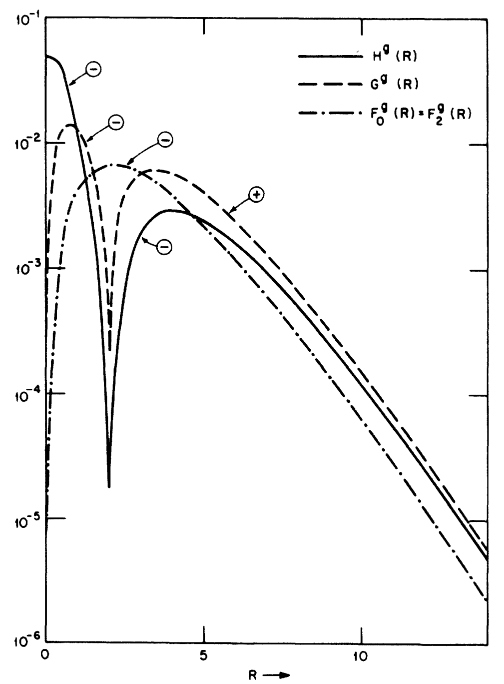

FIG. 3. Second-order contributions to the matrix elements coming from intermediate states in which the helium target remains in its ground state.

$$G^{g}(R)=(-25/64Z^{*3})(1-\tfrac{1}{2}R)Re^{-R} , \qquad (39b)$$

$$H^{g}(R)=(-25/32Z^{*3})(1-\tfrac{1}{2}R)^2e^{-R} . \qquad (39c)$$

For comparison with the other potentials in this section, we have plotted these functions in Fig. 3.

In order to check these approximate expressions, we have also solved Eq. (33) variationally by two different expansions. In one, we used a very simple helium-centered trial function of the form

$$\psi_t=Ae^{-\alpha|\vec{R}-\vec{r}|} ,$$

suitably orthogonalized to remove components of ω_{2s} and ω_{2pm}. Putting such a function into a variational principle, we found results for the quantities in Eqs. (39) which were about 15% smaller in magnitude than those obtained from the Green's-function method given above. A second variational calculation using an expansion in partial waves of the form

$$\psi_t=\sum C_{nl}\,r^nP_l(\cos\theta_{\hat{r}})$$

gave at $R=4$ a result which fell between the helium-centered variational result and the Green's-function result given in Eqs. (39). Since convergence in partial waves is poor for all but very small values of R it was necessary to extrapolate to higher partial waves. These variational results suggest that the results of Eqs. (39) are probably accurate to about 10%.

Up to this point, we have said nothing about the possible effects of the Pauli principle, which we have neglected in the foregoing discussion. To take exclusion into account precisely would be very difficult, so we will attempt to remedy its omission by using a Gombas exchange pseudopotential.[8] This is obtained by treating the electrons as a free-electron gas. Following Gombas, one finds the following simple expression for the effective potential felt by the hydrogen electron:

$$V_{\text{ex}}(\vec{R}, \vec{r})=\tfrac{1}{2}\left[3\pi^2\rho(\vec{R}-\vec{r})\right]^{2/3} ,$$

where ρ is the target electronic charge density. For the simple product wave function we have used, ρ is given by

$$\rho(\vec{R}-\vec{r})=2(Z^{*3}/\pi)\,e^{-2Z^*|\vec{R}-\vec{r}|} ,$$

so that

$$V_{\text{ex}}(\vec{R}, \vec{r})=\tfrac{1}{2}Z^{*2}(6\pi)^{2/3}e^{-4Z^*|\vec{R}-\vec{r}|/3} .$$

To evaluate the exclusion principle corrections to $M_{jj'}$, we will consider

$$M^{\text{ex}}_{jj'}=(\omega_j, V_{\text{ex}}\omega_{j'}) . \qquad (40)$$

This expression is readily evaluated exactly by the same methods used in obtaining $(\phi_j, V\phi_{j'})$. The results for F^{ex}_0, F^{ex}_2, G^{ex}, and H^{ex} are given in Fig. 4. Here F^{ex}_0, F^{ex}_2, G^{ex}, and H^{ex} are defined as usual by

$$M^{\text{ex}}_{2pm',2pm}=\delta_{m'm}F^{\text{ex}}_{0}(R)+A_{m'm}F^{\text{ex}}_{2}(R)$$

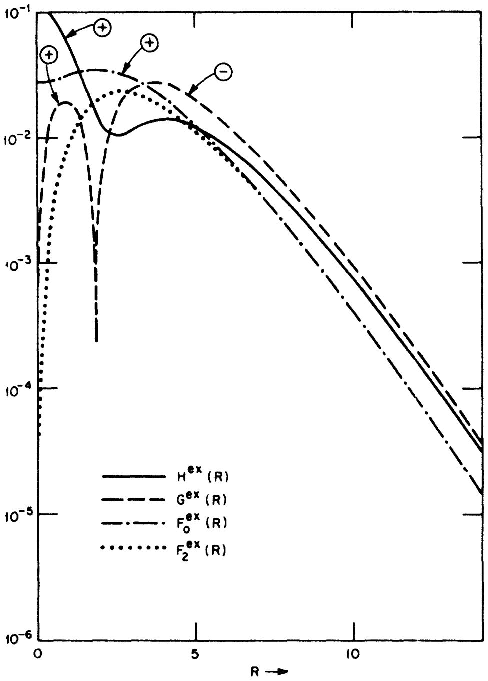

FIG. 4. Exchange contributions to the matrix elements as given by a Gombas exchange pseudopotential.

$$\times\left[\sqrt{\tfrac{4}{5}\pi}\; Y_{2,m-m'}(\theta,\ \phi)\right], \tag{41a}$$

$$M^{ex}_{2s,2pm}=G^{ex}(R)\left[\sqrt{\tfrac{4}{3}\pi}\; Y_{1,m}(\theta,\ \phi)\right], \tag{41b}$$

$$M^{ex}_{2s2s}=H^{ex}(R)\ . \tag{41c}$$

Using the "peaking" approximation, we get the following analytic expression:

$$M^{ex}_{jj'}=(27\pi/16Z^*)(6\pi)^{2/3}\,\omega^*_j(\vec{R})\omega_{j'}(\vec{R})\ . \tag{42}$$

Thus,

$$F^{ex}_0(R)=F^{ex}_2(R)\cong\tfrac{1}{96}(6\pi)^{2/3}R^2e^{-R}\ , \tag{43a}$$

$$G^{ex}(R)\cong\tfrac{1}{16}(6\pi)^{2/3}(1-\tfrac{1}{2}R)Re^{-R}\ , \tag{43b}$$

$$H^{ex}(R)\cong\tfrac{1}{8}(6\pi)^{2/3}(1-\tfrac{1}{2}R)^2e^{-R}\ . \tag{43c}$$

Finally, we can combine all our results, including the Gombas pseudopotential contributions, to write

$$M_{2pm',2pm}=\delta_{m'm}F^T_0(R)+A_{m'm}F^T_2(R)$$

$$\times\left[\sqrt{\tfrac{4}{5}\pi}\; Y_{2,m-m'}(\theta,\ \phi)\right], \tag{44a}$$

$$M_{2s,2pm}=G^T(R)\left[\sqrt{\tfrac{4}{3}\pi}\; Y_{1,m}(\theta,\ \phi)\right], \tag{44b}$$

$$M_{2s2s}=H^T(R)\ , \tag{44c}$$

where

$$F^T_0(R)=f_0(R)+F^e_0(R)+F^g_0(R)+F^{ex}_0(R)\ , \tag{45a}$$

$$F^T_2(R)=f_2(R)+F^e_2(R)+F^g_2(R)+F^{ex}_2(R)\ , \tag{45b}$$

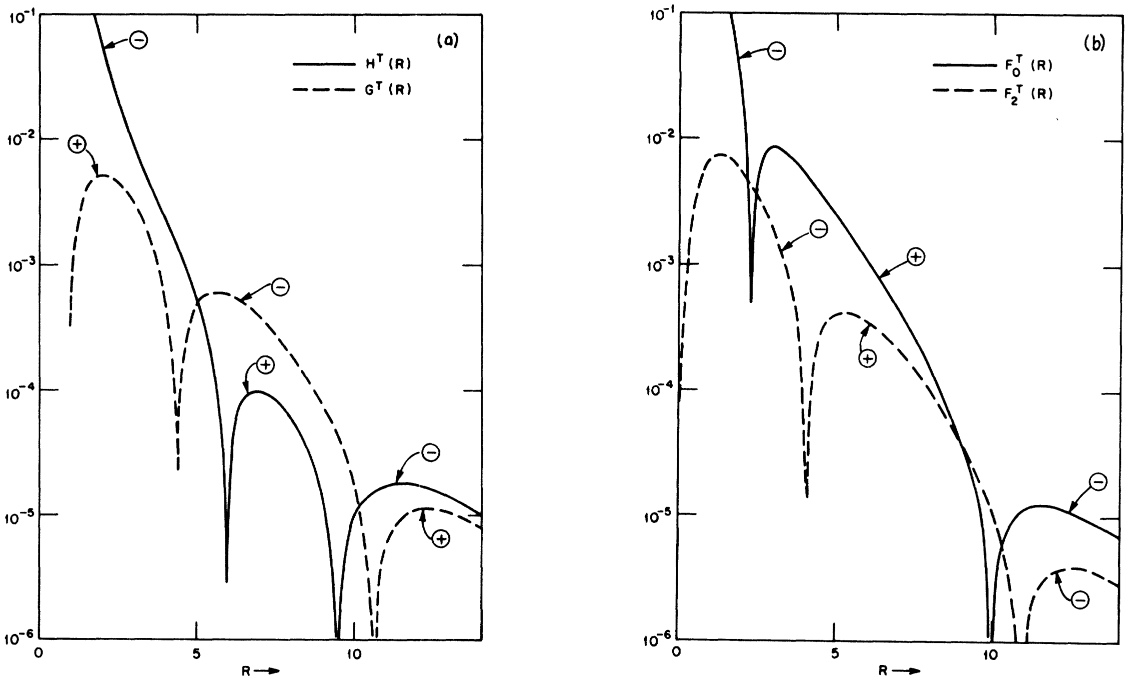

FIG. 5 (a). Total 2s-2s matrix element and total 2s-2p matrix element. (b) $L=0$ and $L=2$ parts of the total 2p-2p matrix element.

$$G^{T}(R) = g(R) + G^{e}(R) + G^{g}(R) + G^{ex}(R) \ , \qquad (45c)$$

$$H^{T}(R) = h(R) + H^{e}(R) + H^{g}(R) + H^{ex}(R) \ . \qquad (45d)$$

These total matrix element contributions, F_0^T, F_2^T, G^T, and H^T are shown in Fig. 5. The most striking aspect of Fig. 5 is the fact that the sum of the four contributions to each curve is much less than any individual contribution. This depends heavily on the inclusion of exchange; without the Gombas contributions, the results for H^T, G^T, F_0^T, and F_2^T would be larger by nearly an order of magnitude over most of the range shown in the figures.

IV. ASYMPTOTIC POTENTIALS

The electrostatic potential energy of Eq. (17) can be expanded in a multipole series which is useful if the internuclear separation is very large. Thus, V consists of a dipole-dipole term

$$V_{dd} = -\sqrt{24\pi} \sum_{a,b,c} \begin{pmatrix} 1 & 1 & 2 \\ a & b & c \end{pmatrix} \mu_a(1)\mu_b(2)\Upsilon_{2c}(\vec{R}) \ , \qquad (46)$$

a dipole-quadrupole term

$$V_{dq} = -\sqrt{60\pi} \sum_{a,b,c} \begin{pmatrix} 1 & 2 & 3 \\ a & b & c \end{pmatrix} [\mu_a(1)q_b(2) - \mu_a(2)q_b(1)] \times \Upsilon_{3c}(\vec{R}) \ , \qquad (47)$$

plus higher-order terms. The above two terms will suffice for the remainder of our discussion. In Eqs. (46) and (47), $\mu_a(i)$ refers to the dipole operator for atom i, while $q_b(i)$ represents the quadrupole tensor operator. The irregular solution to Laplace's equation $R^{-l-1}Y_{lm}(\hat{R})$ has been denoted by $\Upsilon(\vec{R})$.

According to the discussion of Sec. III, we must investigate the large-R behavior of the matrix elements of the effective interaction

$$\mathcal{V} = \sum_n \sum_l \frac{V|n,l\rangle\langle n,l|V}{E_0 - E_l + E_2 - E_n} \ . \qquad (48)$$

The index n denotes the totality of hydrogen states, while l represents the spectrum of states of the target. Omitted from the sum is that term for which n and l refer simultaneously to the hydrogen $2s$ or $2p$ state and the target ground state which is assumed to be an s state. The energy corresponding to the former state has been denoted by E_2 and that corresponding to the latter state by E_0.

Since collision durations are typically several orders of magnitude smaller than fine-structure, hyperfine, or Lamb-shift periods we shall neglect these details and take H_1 to be a spinless, nonrelativistic Hamiltonian. As mentioned previously, we are concerned with the matrix elements of $\mathcal{V}$ responsible for connecting the $2s$ to the $2p$ state. Since these are states of opposite parity, the portion of $\mathcal{V}$ causing such transitions must also have odd parity. Thus $\mathcal{V}$ must be linear in both V_{dd} and V_{dq}. The dipole operator acts twice on the target atom but only once on the hydrogen atom. By parity and angular momentum considerations it follows that the only terms contributing to the l sum are P states. Similarly only P and D states are included in the n summation. The sum may therefore be decomposed into a contribution from the $2p$ state and a contribution from all other excited states

$$\mathcal{V} = \mathcal{V}_1 + \mathcal{V}_2 \ ,$$

$$\mathcal{V}_1 = \sum_{l}{}' \frac{V|2p,l\rangle\langle 2p,l|V}{E_0 - E_l} \ ,$$

$$\mathcal{V}_2 = -\frac{2}{\pi}\int_{0^+}^{\infty} V \frac{E_0 - H_2}{(E_0 - H_2)^2 + \omega^2} \, \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} \, V d\omega \ .$$

In the first sum, the prime indicates that we omit the helium ground state from the summation. In the second sum we have used closure and the following integral identity[9] (valid for $a < 0$, $b < 0$):

$$\frac{1}{a+b} = -\frac{2}{\pi}\int_0^{\infty} \frac{a}{a^2+\omega^2} \, \frac{b}{b^2+\omega^2} \, d\omega \ .$$

The techniques used for evaluating $\mathcal{V}_1$ and $\mathcal{V}_2$ are somewhat different, so they will be discussed independently. One notes that the only nonvanishing contribution to the matrix element is when V_{dd} acts on the $2s$ state to form an intermediate p state, which is subsequently operated on by V_{qd} to form the final $2p$ state. Thus, we have

$$\langle f|\mathcal{V}_1|i\rangle = \sum_l{}' \sum_m \langle 2p^{\mu}, 0|V_{qd}|2p^m, l\rangle \times \langle 2p^m, l|V_{dd}|2s, 0\rangle (E_0 - E_l)^{-1} \ .$$

The aximuthal quantum numbers of the intermediate and final states have been included explicitly in the above equation. Equations (46) and (47) are then combined with the above expression and the following formulas are used to simplify it[10]:

$$\langle 2p^{\mu}|q_{\beta}(1)|2p^m\rangle = (-)^{1-\mu}\begin{pmatrix} 1 & 2 & 1 \\ -1 & \beta & m \end{pmatrix}\langle 2p||q||2p\rangle = 12(-)^{1-\mu}\begin{pmatrix} 1 & 2 & 1 \\ -\mu & \beta & m \end{pmatrix} \ ,$$

$$\langle 2p^m|\mu_a(1)|2s\rangle = (-)^{1-m}\begin{pmatrix} 1 & 1 & 0 \\ -m & a & 0 \end{pmatrix}\langle 2p||\mu||2s\rangle = -3\delta_{ma} \ ,$$

$$\sum_{abc,\beta\gamma} (-)^{b+1+\mu}\begin{pmatrix} 1 & 1 & 2 \\ a & b & c \end{pmatrix}\begin{pmatrix} 1 & 2 & 3 \\ -b & \beta & \gamma \end{pmatrix}\begin{pmatrix} 1 & 2 & 1 \\ -\mu & \beta & a \end{pmatrix} \times \Upsilon_{2c}(\vec{R})\Upsilon_{3\gamma}(\vec{R}) = -\left(\frac{35}{12\pi}\right)^{1/2}\begin{pmatrix} 1 & 2 & 3 \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} 2 & 3 & 1 \\ 2 & 1 & 1 \end{Bmatrix}\frac{Y_{1\mu}^{*}(\vec{R})}{R^7} \ .$$

Thus, we have

$$\langle f | \mathcal{V}_1 | i \rangle = +108\sqrt{3\pi}\ \alpha(0)\, Y^*_{1\mu}(\hat{R})/R^7 ,$$

where $\alpha(0)$ is the static polarizability of the target atom

$$\alpha(0) = 2{\sum_l}' \langle 0 | \mu_0 | l \rangle \langle l | \mu_0 | 0 \rangle (E_l - E_0)^{-1} .$$

Applying similar angular momentum techniques to $\mathcal{V}_2$ yields the following expression:

$$\langle f | \mathcal{V}_2 | i \rangle = -40 \left(\frac{7}{2\pi}\right)^{1/2} \begin{pmatrix} 1 & 2 & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} 2 & 3 & 1 \\ 2 & 1 & 1 \end{Bmatrix} \frac{Y^*_{1\mu}(\hat{R})}{R^7} f$$

$$= -\left(\frac{96}{5\pi}\right)^{1/2} f \frac{Y^*_{1\mu}(\hat{R})}{R^7} ,$$

where

$$f = \int_{0^+}^{\infty} \left\langle 0 \right\| \mu \frac{E_0 - H_2}{(E_0 - H_2)^2 + \omega^2} \mu \left\| 0 \right\rangle \times \left\{ \left\langle 2p \right\| \mu \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} q \left\| 2s \right\rangle + \left\langle 2p \right\| q \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} \mu \left\| 2s \right\rangle \right\} d\omega . \tag{49}$$

The first factor can be related to the dynamic polarizability of the target atom evaluated at imaginary frequencies

$$\left\langle 0 \right\| \mu \frac{E_0 - H_2}{(E_0 - H_2)^2 + \omega^2} \mu \left\| 0 \right\rangle = \tfrac{1}{2}\sqrt{3}\ \alpha(i\omega).$$

Expressions for $\alpha(i\omega)$ have been given by several authors[11] for a number of atoms. Usually they take the form

$$\alpha(i\omega) = \sum_{i=1}^{M} \frac{f_i}{\omega_i^2 + \omega^2} ,$$

where M is some finite number. The $\{\omega_i\}$ represent a set of pseudoresonance frequencies and the $\{f_i\}$ a set of pseudo-oscillator strengths, which are determined by a variational principle, or by relating them to generalized oscillator strengths, or even by direct numerical fits to spectroscopic data.

The problem is thus reduced to evaluating the matrix elements contained in the brackets of Eq. (49). We shall coin the word "quenchability" when referring to this quantity, since it is a measure of the propensity of the hydrogen atom to be quenched. It will be denoted by $Q(\omega)$. We begin by considering the first term of the quenchability. We write

$$\left\langle 2p \right\| q \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} \mu \left\| 2s \right\rangle = -\sqrt{\tfrac{15}{2}}\, \langle 2p^0 | q | x \rangle , \tag{50}$$

where

$$| x \rangle = \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} \mu \,| 2s \rangle . \tag{51}$$

Using a well-known technique[12,13] evaluation of $|x\rangle$ can be accomplished by solving the inhomogeneous equation

$$[(E_2 - H_1^1)^2 + \omega^2]\Phi = (-r + \tfrac{1}{4} r^2) e^{-r/2} , \tag{52}$$

where

$$H_1^1 = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{1}{r} , \quad | x \rangle = -(8\pi)^{-1/2} \frac{\Phi}{r} \cos\theta .$$

This, in turn, may be solved by a variational procedure using a trial wave function of the Sturmian form

$$\Phi(r) = r^2 e^{-r/2} \textstyle\sum_n c_n r^n . \tag{53}$$

The procedure is straightforward and will not be duplicated here. Having solved for the c_n we then have

$$\left\langle 2p \right\| q \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} \mu \left\| 2s \right\rangle = -\tfrac{1}{30}\sqrt{\tfrac{15}{2}} \sum_n (n+6)!\, c_n . \tag{54}$$

One may apply an analogous technique to the second term in the quenchability.

The quenchability has been computed for a range of frequencies and is plotted in Fig. 6. Twenty terms were included in the trial wave functions and the algebraic manipulations were performed on a digital computer. Gaussian elimination was employed to obtain the c and d vectors. The matrix elements computed converged to the asymptotic values

$$\left\langle 2p \right\| q \frac{E_2 - H_1}{(E_2 - H_1)^2 + \omega^2} \mu \left\| 2s \right\rangle \xrightarrow[\omega \to \infty]{} -(30)^{1/2} \omega^{-2} ,$$

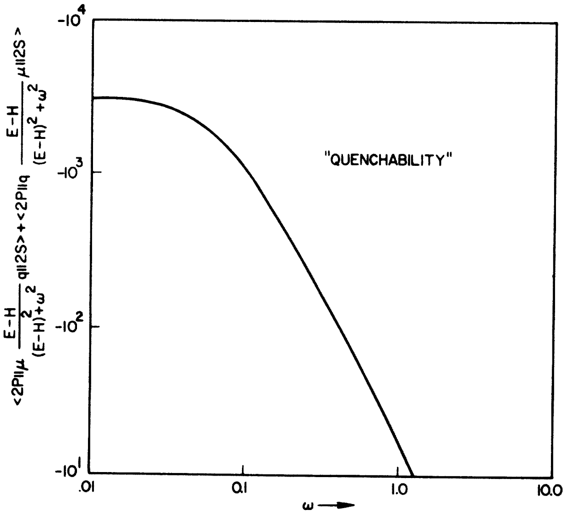

FIG. 6. Dynamic quenchability $Q(w)$ of metastable hydrogen.

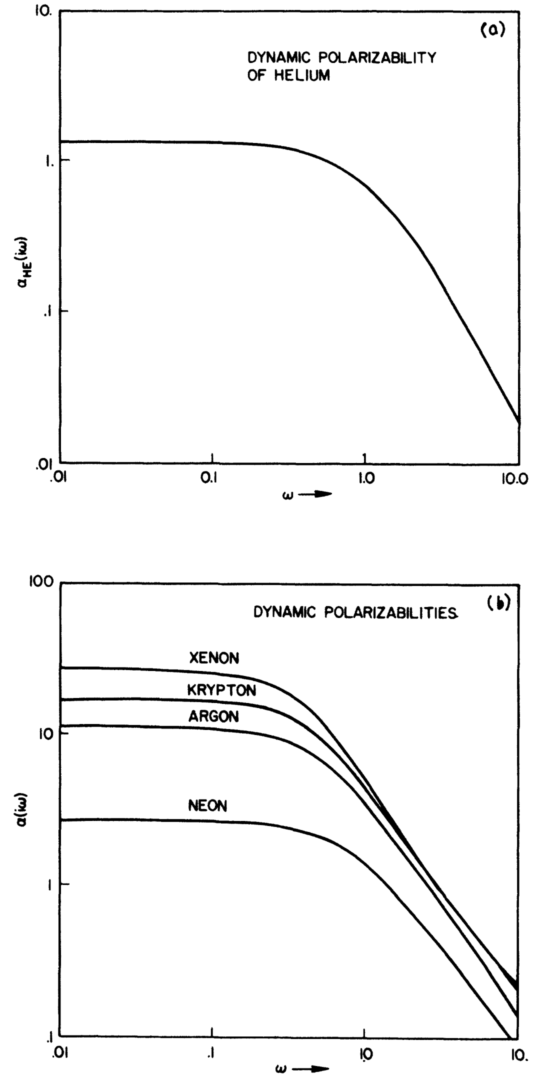

FIG. 7. (a) Dynamic polarizability of helium. (b) Dynamic polarizability of the other noble gases.

$$\left\langle 2p \left\| \mu \frac{E_2-H_1}{(E_2-H_1)^2+\omega^2}\, q \right\| 2s \right\rangle \xrightarrow[\omega\to\infty]{} -(120)^{1/2}\,\omega^{-2} .$$

The integration of Eq. (49) may now be done numerically. In Fig. 7 we have plotted $\alpha(i\omega)$ for several rare gases. The final result is

$$\langle f | \mathcal{V} | i \rangle = -C\, Y^*_{1\mu}(\hat{R})/R^7 ,$$

where

$$C = -108\,(3\pi)^{1/2}\,\alpha(0) + (72/5\pi)^{1/2} \int_{0^+}^{\infty} \alpha(i\omega) Q(\omega)\, d\omega . \tag{55}$$

Values of $\alpha(0)$ and C appear in Table I for the rare gases. Comparing the value of C obtained from Table I for helium with the result of Eq. (28b) we find that $\Delta = -1.09$.

In Fig. 8 we have plotted the quantity

$$\left\langle 2s \left| \mu_0 \frac{E_2-H_1}{(E_2-H_1)^2+\omega^2}\, \mu_0 \right| 2s \right\rangle = -\tfrac{1}{2}\, \alpha_H{}^*(i\omega) ,$$

which is the dynamic polarizability of metastable hydrogen (up to a factor). The Van der Waals interaction may be written as[9] a fold of the two polarizabilities,

$$\mathcal{U}_1(2s) = -(3/\pi R^6) \int_0^{\infty} \alpha_H{}^*(i\omega)\,\alpha(i\omega)\, d\omega ,$$

plus a contribution due to the $2p$ state

$$\mathcal{U}_2(2s) = -\frac{3}{2R^6} \sum_l{}' \frac{f_{2s\text{-}2p}(1)}{E_{2s}-E_{2p}} \frac{f_l(2)}{E_l-E_0} , \tag{56}$$

where $f_{2s\text{-}2p}$ is the oscillator strength for a $2s$-$2p$ transition and f_l is the corresponding strength for a 0 to l transition in the target. The expression in Eq. (56) reduces to

$$\mathcal{U}_2(2s) = -27\,\alpha(0)/R^6 ,$$

which just involves the static polarizability of the target. For the case of helium,

$$\mathcal{U} = \mathcal{U}_1 + \mathcal{U}_2 = -\frac{18.75}{R^6} - \frac{35.48}{R^6} = -\frac{54.26}{R^6} .$$

Comparing this result with that of Eq. (29a) again yields $\Delta = -1.09$ for the average energy denominator, in agreement with the result obtained from Eq. (55).

V. PSEUDOPOTENTIAL APPROACH

Having discussed in the previous sections a perturbation approach to obtaining the quenching matrix elements we now turn our attention to a semiphenomenological model. There are two characteristics of the metastable hydrogen-helium system which deserve attention. First of all, the hydrogen atom is much larger than the helium atom. Thus, the maximum in the helium charge distribution occurs at $r = 1/Z^* = \frac{16}{27}$, while for metastable hydrogen the dominant maximum occurs at about $r = 5$. This suggests that it might be possible to replace the helium atom by a localized potential of some sort, especially when the two atoms are well separated ($R \gtrsim 5$). The second noteworthy feature is that the energy of the electron is only $-\frac{1}{8}$ a.u. below the continuum. Thus the hydrogenic electron can be

TABLE I. Tabulation of parameters of the effective interaction for the rare gases.

Gas	$\alpha(0)$	C
He	1.3799	−1412.6
Ne	2.6667	−2815.4
Ar	11.0863	−11418
Kr	16.7765	−17112
Xe	27.0718	−27118

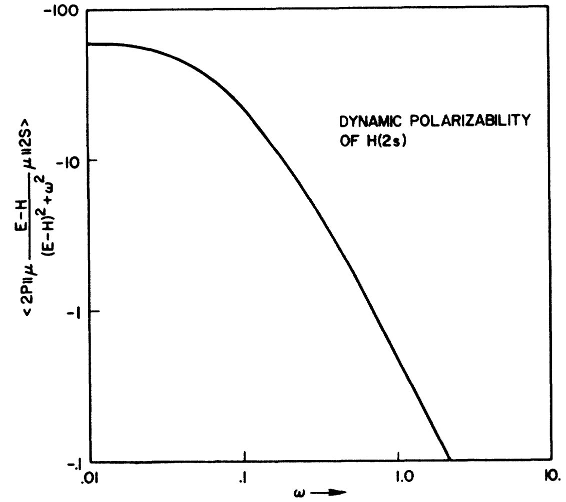

FIG. 8. Dynamic polarizability of metastable hydrogen.

regarded almost as a zero-energy electron. We therefore suspect that an essential ingredient in our theory will be scattering length for electron-helium scattering. This quantity has been the object of extensive experimental[14] and theoretical research.[15] The value we shall use is the one obtained by Bransden and McDowell[14] and is $a = 1.1a_0$. We therefore combine the above-mentioned properties and introduce a Breit-Fermi pseudopotential to replace the helium atom:

$$V_{\mathrm{BF}}\,\psi = 2\pi a\,\delta(\vec{\rho})\frac{\partial}{\partial\rho}(\rho\psi)\ .$$

For a nonsingular wave function, this reduces simply to $2\pi a\,\delta(\vec{\rho})\psi$. This type of pseudopotential has been employed in nuclear physics[16] and statistical physics[17] but does not seem to have been of much use before in atomic physics.

Unfortunately, the electron is not the only entity interacting with the helium atom, since the proton is also nearby. We thus have to account for the polarization effect produced by the proton. To do this we refer back to the polarizable sphere model discussed earlier. From Eq. (30) we have a polarization interaction

$$U = -\frac{1}{2}\frac{\alpha}{R^4} - \frac{1}{2}\frac{\alpha}{|\vec{R}-\vec{r}|^4} + \alpha\frac{\hat{R}\cdot(\vec{R}-\vec{r})}{R^2|\vec{R}-\vec{r}|^3}\ . \tag{57}$$

The first term does not connect the $2s$ state to the $2p$ state and so is relatively uninteresting. The second term represents the polarization interaction of the electron with the helium atom. This term is one of the ingredients that goes into a calculation of the electron-helium scattering length. Thus, by using a pseudopotential, we have in effect included it. The pseudopotential of course contains in addition exchange and penetration contributions, but these need not be calculated since we take a to be given by experiment. The final term represents a cross-polarization term. It is nonsingular enough at $\vec{R}=\vec{r}$ to be evaluated in first-order perturbation theory without the use of a cutoff.

Let us now compare the matrix elements of the Breit-Fermi pseudopotential with those of the cross-polarization potential. The matrix elements of the pseudopotential are given simply, in our familiar notation, by

$$f_0^{\mathrm{BF}}(R) = f_2^{\mathrm{BF}}(R) = \tfrac{1}{48}aR^2e^{-R}\ , \tag{58a}$$

$$g^{\mathrm{BF}}(R) = \tfrac{1}{8}aR(1-\tfrac{1}{2}R)e^{-R}\ , \tag{58b}$$

$$h^{\mathrm{BF}}(R) = \tfrac{1}{4}a(1-\tfrac{1}{2}R)^2e^{-R}\ . \tag{58c}$$

These are of the same form as the first-order potentials and are plotted in Fig. 9.

The cross-polarization potential, given by the last term in Eq. (57), can be written as

$$U_{\mathrm{CP}} = \frac{\alpha}{R^2}\frac{\hat{R}\cdot(\vec{R}-\vec{r})}{|\vec{R}-\vec{r}|^3} = -\frac{\alpha}{R^2}\frac{d}{dR}\frac{1}{|\vec{R}-\vec{r}|}\ .$$

Thus, the matrix elements of U_{CP} involve only matrix elements of the Coulomb potential, which are trivial to evaluate. For example, we find for the $2s$-$2p$ matrix element

$$g^{\mathrm{CP}}(R) = -\frac{6\alpha}{R^5} + \alpha\left[\frac{6}{R^5}+\frac{6}{R^4}+\frac{3}{R^3}+\frac{1}{R^2}+\frac{1}{4R}+\frac{1}{8}\right]e^{-R}\ ;$$

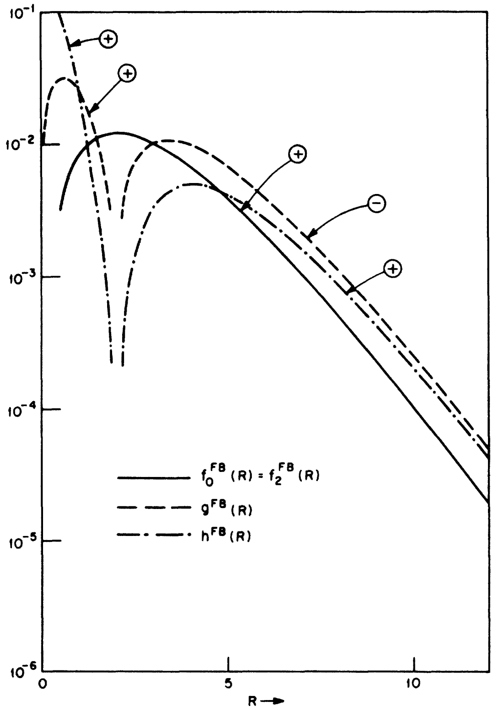

FIG. 9. $2s$-$2s$, $2s$-$2p$, and $2p$-$2p$ matrix elements calculated using a Breit-Fermi pseudopotential.

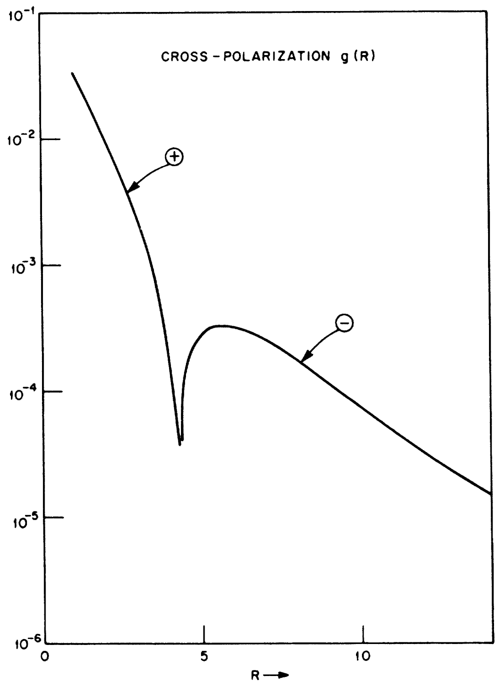

FIG. 10. Cross-polarization contribution to the $2s$-$2p$ matrix element.

while for the diagonal $2s$-$2s$ element we have

$$h^{\mathrm{CP}}(R)=\frac{\alpha}{R^4}-\alpha\left[\frac{1}{R^4}+\frac{1}{R^3}+\frac{1}{2R^2}+\frac{1}{8}\right]e^{-R}\,.$$

Similar expressions can be obtained for the $2p$-$2p$ matrix elements. However, the point to notice is that these cross-polarization matrix elements are small compared to the pseudopotential matrix elements for all important distances. To show this, we have plotted $g^{\mathrm{CP}}(R)$ in Fig. 10. Comparing this curve with $g^{\mathrm{BF}}(R)$ shown in Fig. 9, we see that $g^{\mathrm{CP}}(R)$ represents only a small correction to $g^{\mathrm{BF}}(R)$, and we will neglect it in what follows. Similar conclusions hold for the other, less important, matrix elements.

Of course, we know that at very large internuclear separations the pseudopotential model cannot be correct because the f, g, and h parameters do not take on the correct asymptotic values. However, we shall see that the cross section is determined not by large R values but by intermediate R values, where the asymptotic potentials are of little consequence. Thus we might expect a reasonable approximation to the true matrix elements by this method.

VI. QUENCHING CROSS SECTIONS

Having obtained the elements of the matrix $M_{nn'}$ of Eq. (16) in two different approximations it remains only to solve Eq. (15b). This equation defines a set of four coupled first-order differential equations in the variable Z. The impact parameter b is merely a label so far as the actual solution of the equations is concerned. Furthermore, we need a solution to Eq. (15b) only for $Z\rightarrow\infty$, not for all Z.

In the case of the perturbation-theory potentials, which are significantly smaller in magnitude than the Breit-Fermi potentials, we integrated Eq. (15b) by using a standard Adams-Moulton technique. This was done for a large range of impact parameters. Then

$$\sigma_Q=2\pi\int_0^{\infty}\left[\sum_{m=-1}^{1}\left|\alpha_{2pm}^{(2s)}(b,\,Z=\infty)\right|^2\right]b\,db \qquad (59)$$

was evaluated by numerical integration. It should be noted that although the elements of $M_{nn'}$ depend on ϕ [see, for example, Eqs. (21), (28), (39), (43), and (44)], one can readily show that $\alpha_{2pm}^{(2s)}$ is proportional to $e^{-im\phi}$, so that the expression under the integral in Eq. (59) is independent of ϕ. Actually, because of the factor $1/v$ in Eq. (15b), it happens that for small impact parameters and moderately small values of v, the integrand of Eq. (59) oscillates quite rapidly. Rather than waste computer time in this case, we merely obtained an average value of

$$\sum_{m=-1}^{1}\left|\alpha_{2pm}^{(2s)}(b,\,Z=\infty)\right|^2$$

(roughly equal to $\frac{1}{2}$) in the region of rapid oscillation and multiplied this average value by πb_c^2, where b_c is the impact parameter at which the above quantity

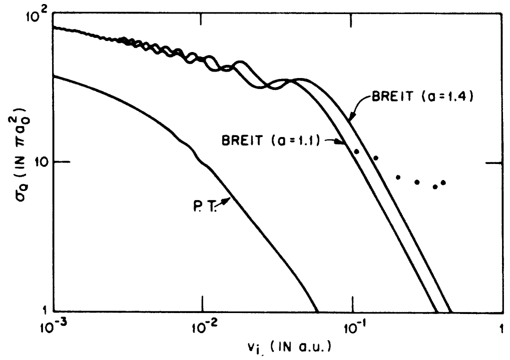

FIG. 11. Lower curve represents the values of the quenching cross section obtained from perturbation theory matrix elements; the two upper curves correspond to values of the quenching cross section obtained by using a Breit-Fermi pseudopotential. One was calculated using an e+He scattering length equal to 1.1 a.u., which seems to be the best experimental value; the other used $a=1.4$ a.u. to give an idea of the sensititivity of the results to variations in the scattering length. The data are experimental values from Byron, Krotkov, and Medeiros (Ref. 6).

begins to oscillate rapidly. All numerical checks which we performed indicated that such a procedure should produce errors of no more than 5% in σ_Q. The results are shown in the bottom curve in Fig. 11.

The one risk that is run in this method is that one may miss small-scale oscillatory structure in the total cross section. To illustrate how this might come about, let us obtain σ_Q for the Breit-Fermi model. Here the matrix elements have a simple form, so we can analyze them in analytical detail. To begin with let us note that it is not a bad approximation to say on physical grounds that the value of σ_Q is largely determined by the impact parameter at which one first gets a unit probability of transition, and this in turn will depend primarily on the $2s$-$2p$ matrix element. Let us therefore set all other matrix elements equal to zero (i.e., $H^T = F_0^T = F_2^T = 0$). Furthermore, the $2s$-$2p_0$ matrix element is expected to be unimportant because it is an odd function of Z as one integrates through the interaction region (remember that $\sin\theta = b/R$ and $\cos\theta = Z/R$). We will also set this matrix element equal to zero. With all these approximations, the matrix $M_{nn'}$ commutes with itself for different values of Z, so Eq. (15b) is solved simply by

$$\alpha^{(2s)} = \left\{\exp\left[-(i/v)\int_{-\infty}^{\infty} M\,dZ\right]\right\}\alpha^{(2s)}(Z=-\infty)\ , \tag{60}$$

where we have written the result in matrix form as in Eq. (15a). According to the boundary condition, we have

$$\alpha^{(2s)}(Z=-\infty) = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}\ .$$

This expression for $\alpha^{(2s)}$ can be simplified greatly by using the method of Byron and Foley[18] and noting that the integral along Z of the $2s$-$2p$ matrix elements can be done analytically in terms of Bessel functions since $R = (b^2+Z^2)^{1/2}$:

$$\int_{-\infty}^{\infty}(1-\tfrac{1}{2}R)R\sin\theta\, e^{-R}dZ = b\int_{-\infty}^{\infty}(1-\tfrac{1}{2}R)e^{-R}dZ$$

$$= b^2[K_1(b) - bK_0(b)]\ .$$

Using this result along with Eq. (58b), we have from Eq. (57)

$$\alpha^{(2s)}(b) = \exp i\begin{bmatrix} 0 & A/\sqrt{2} & 0 & -A/\sqrt{2} & 1 \\ A/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ -A/\sqrt{2} & 0 & 0 & 0 & 0 \end{bmatrix}, \tag{61}$$

where

$$A = (a/8v)\,b^2[K_1(b) - bK_0(b)]\ . \tag{62}$$

Diagonalizing the matrix inside the exponential of Eq. (61) and resynthesizing outside the exponential, we find for σ_Q

$$\sigma_Q = 2\pi\int_0^{\infty}\sin^2\{(a/8v)b^2[K_1(b) - bK_0(b)]\}\,b\,db\ . \tag{63}$$

The two upper curves in Fig. 11 show σ_Q as a function of v for two different scattering lengths. The oscillatory structure, although only at the 5–10% level, is very marked. The reason for its appearance is easily understood by looking at Eq. (63) for σ_Q. The argument of the sine is a function which takes on two extrema, one at $b \cong 3.2$, the other at $b \cong 0.5$. Because of the smallness of the impact parameter, the second extremum will be unimportant. The argument of the sine becomes large as v becomes small so that one can use the method of steepest descent to evaluate the integral in Eq. (63) in the vicinity of the extremum at $b = b_e = 3.2$. Doing this, we find that σ_Q can be written (in units of πa_0^2) as

$$\sigma_Q(v) = \sigma_Q^0(v) - A\sqrt{v}\,\cos(B/v + \tfrac{1}{4}\pi)\ , \tag{64}$$

where

$$A = \left(\frac{16\pi b_e^2}{a[6b_e^2K_1(b_e) - 9b_eK_0(b_e) - b_e^3K_0(b_e)]}\right)^{1/2} \simeq \frac{45}{\sqrt{a}}\ ,$$

$$B = \tfrac{1}{4}ab_e^2[K_1(b_e) - b_eK_0(b_e)] \simeq -0.145a\ ,$$

and $\sigma_Q^0(v)$ is a smoothly varying function of v which increases gradually as v decreases. For $v \lesssim 0.01$, $\sigma_Q^0(v)$ is approximately equal to $\frac{1}{2}b_c^2 + (\frac{1}{2}\pi)^2 b_c$, where b_c is the largest impact parameter for which we have

$$(a/8v)b^2[K_1(b) - bK_0(b)] \simeq \tfrac{1}{2}\pi\ .$$

Equation (64) is meaningful only when $b_c > b_e$.

In practice, one may expect that the small oscillations in σ_Q will be washed out when all the other elements of $M_{nn'}$ are included, and a detailed numerical investigation bears this out. The expression for $P(b)$ under the integral in Eq. (63) varies very slowly in a region of about 1 a.u. around $b_e = 3.2$ (for, say, $v \simeq 0.01$), whereas it varies very rapidly as one gets outside this region. This is, in fact, the conceptual basis behind the method of steepest descent used above. However, the quantity $P(b)$ obtained by numerically integrating the basic equations with all matrix elements present varies just as rapidly in the vicinity of b_e as it does in any other region of impact parameter space. Thus, no oscillatory structure of any significance is expected in practice. One aspect of the exact solution which is expected to differ from the upper curves in Fig. 11 is that the exact $P(b)$ will not oscillate with an average value of $\frac{1}{2}$, but rather with a somewhat larger value, so that the true quenching cross section will be larger than those shown for the Breit-Fermi case. A computation for $v = 0.01$

gave a cross section about 20% larger than the approximate result. Deviations are expected to be generally of this order of magnitude below $v \simeq 0.01$, becoming less significant as one goes to larger velocities.

It should perhaps be remarked that the oscillations in the approximate Breit-Fermi cross sections have an origin quite similar to those that occur in low-energy atom-atom elastic scattering. In the latter case, it is the scattering phase shift which has a stationary point as a function of impact parameter, while in the former case it is the $2s$-$2p$ transition probability which shows this behavior.

VII. DISCUSSION

In the analysis presented above, we have assumed that the quenching of metastable hydrogen is due entirely to transitions to the $2p$ state. This assumption becomes valid at velocities sufficiently small so that $\Delta E/v \gtrsim 1$ (in a.u.), where ΔE is the energy difference between $H(2s)+He(1s^2)$ and $H(3s)+He(1s^2)$. As $\Delta E/v$ starts to become comparable to 1, then excitation of $H(2s)$ to other hydrogen states with subsequent cascade to the ground state begins to contribute to the quenching of $H(2s)$, and at slightly higher velocities ionization begins to play a role. In fact, at velocities so large that the Born approximation is valid, Byron, Krotkov, and Medeiros[6] have shown that $2s$-$2p$ transitions play a very minor role in quenching $H(2s)$. Thus, for example, in the energy range $E > 250$ eV one will obtain different cross sections depending on whether one counts Lyman-alpha protons from the interaction region or whether one detects directly the depletion of the $H(2s)$ beam. The difference between these two cross sections essentially measures the ionization of $H(2s)$. At energies below about 250 eV, these two cross sections should be the same.

In this paper, we have attempted two different approaches to the calculation of the quenching matrix elements. The first was a perturbation-theory approach. The total matrix element was taken to be the sum of the first-order electrostatic potential, the second-order electrostatic potential (i.e., the helium atom is clamped in its ground state so it is effectively just a charge distribution), the long-range second-order potential (the helium atom is in an excited intermediate state) evaluated in the Unsold approximation, and finally a Gombas exchange term to mimic the effects of the Pauli exclusion principle. A large amount of cancellation was found between the various contributions, so that the magnitude of the resultant matrix elements depends very sensitively on just how good the various approximations are. In particular, we might expect significant deviations for the exchange potential since it is based on an electron-gas model of the helium atom. Also, the assumption that the average energy denominator in the Unsold approximation is independent of internuclear separation must be subject to scrutiny. Errors of the order of 25% in either the exchange matrix elements or the Unsold matrix elements could lead to total quenching matrix elements whose associated quenching cross sections would be in reasonable agreement with experiment[6] at around 300 eV.

We should point out, however, that this same method applied to the ground state of hydrogen, i.e., to $H(1s)+He(1s^2)$, does not exhibit such extensive cancellation, except in the region where the attractive potential tail goes over into the repulsive potential core. Comparing the results obtained by this method[19] with those found by Hartree-Fock-LCAO techniques[20] one finds that at distances larger than about $R = 3$ the perturbation approach gives more plausible results than does Hartree-Fock-LCAO, since the perturbation method gives a much more satisfactory account of the attractive tail of the potential. This is due to the fact that many intermediate states are necessary to get the long-range effects in the H + He system.

Our second method of attack was able to circumvent some of the pitfalls of the former approach. The target atom was replaced by a pseudopotential characterizing the electron-target interaction as determined by low-energy e-He elastic scattering. Thus, we were able to avoid the calculation of the various electron-atom interactions by introducing the experimental scattering length. The pseudopotential was then allowed to perturb the hydrogen atom and the quenching matrix elements were computed using lowest-order perturbation theory.

It would be surprising if either of these two approaches gave useful results at energies much greater than 250 eV ($v > 0.1$ a.u.) since in this energy region the cross section will be determined by quenching matrix elements at small values of the internuclear separation, say $R < 4$. Here the atoms are beginning to overlap rather extensively and the above pictures undoubtedly fail. Also, transitions to states other than $H(2p)$ begin to play a role as we go to the region above $v = 0.1$. However, it is interesting to note that just at the edge of this region, namely, at 300 eV the data of Byron *et al.*[6] agree quite well with the pseudopotential results as shown in Fig. 11. It is also reassuring to see the $2s$-$2p$ cross section falling *below* the experimental results as more quenching processes become important. In order to test the above calculations convincingly, however, it would be desirable to have experimental results below 250 eV. The thermal region ($v \simeq 0.001$) and the region around 2.5 eV ($v \simeq 0.01$) would seem to be the most promising possibilities.

Finally, we should perhaps comment on several alternative theoretical approaches. We have already mentioned coupled-state and Hartree-Fock formalisms in connection with the H(1s) + He(1s^2) systems, where we believe that at all but rather small internuclear separations such methods are unreliable. This is even more likely to be the case in the problem under discussion, where in addition to questions concerning the adequacy of the large-R behavior of molecular energy curves there will be even more serious doubts about the wave functions which must be used to calculate the matrix elements coupling the 2s and 2p states. An approach related somewhat to our own has been given by Byron *et al.*,[6] who attempt to explain their results in the region $300 < E < 4500$ eV by using an effective potential of the polarization type in an eikonal calculation (which includes an infinite number of final states). In view of the important role played by exchange in our perturbation calculations, the agreement between theory and experiment found by Byron *et al.* would appear to be fortuitous, although it indeed seems likely that a considerable range of final states must be considered in order to explain[21] the results of Byron *et al.* in the keV region.

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