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Velocity-Dependent Orbitals in Proton-On-Hydrogen-Atom Collisions*

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Requirements are outlined for a suitable set of dynamic orbitals for theoretical studies in collision problems. The effect of these upon the wave function, dynamic energy correction, and effective internuclear potential are all considered. It is shown that earlier forms suggested for this type of problem do not meet all required dynamic boundary conditions, principally because of their failure to recognize that physically, for moderate speed collisions, the electron at times "belongs" to the "molecule" proper and not to either atom individually. The earlier orbitals also fail to make allowances for the reluctance of an electronic charge distribution to follow rapid rotation of an internuclear axis. These considerations suggest a new form of dynamic orbital which by remedying these deficiencies automatically achieves complete orthonormality. The results of preliminary charge transfer calculations with the new orbital basis are presented.

I. INTRODUCTION

There have been many attempts,[1,2] recently some notably successful ones,[3,4] at a theoretical verification of the remarkable differential cross-section data of Everhart *et al.*[5] for charge exchange in the proton-on-hydrogen-atom system. One result of all these efforts has been the emergence of two clear shortcomings of the original method of perturbed stationary states (pss) proposed by Bates, Massey, and Stewart.[6] These are (1) failure of the theory to account, in charge transfer processes, for transfer of the momentum of the electron and (2) failure of the theory to account for the reluctance of electronic eigenfunctions to follow the rotation of an internuclear line in even moderate speed collisions. Both of these failures are due to the inability of the theory to account for velocity-dependent effects caused by the presumably small, yet finite, relative velocity of the colliding particles and both enter into the mathematics of the theory through the form chosen for the electronic basis functions. Bates and McCarroll[7] showed that the first of the above difficulties was related to the inability of an adiabatic basis to match the correct asymptotic form for the system wave function and suggested the use of "traveling orbitals" which differed from their static counterparts by the inclusion of a velocity-dependent exponential factor. Thus for a homonuclear system such as the one under discussion, they suggested the use of gerade (+) and ungerade (−) basis functions of the form

$$\Phi_n^{\pm}(\vec{r}, t) = \tfrac{1}{2}\{[\chi_n^{+}(\vec{r}, \vec{R}) + \chi_n^{-}(\vec{r}, \vec{R})]e^{-im\vec{V}\cdot\vec{r}/2\hbar} \pm [\chi_n^{+}(\vec{r}, \vec{R}) - \chi_n^{-}(\vec{r}, \vec{R})]e^{im\vec{V}\cdot\vec{r}/2\hbar} \times \exp\{-(i/\hbar)\int[\epsilon_n^{\pm}(R) + \tfrac{1}{2}m(v/2)^2]\,dt\}. \quad (1)$$

Here the $\chi_n^{\pm}$ represent static molecular electronic eigenfunctions (or approximations thereto), $\vec{r}$ and $\vec{R}$ are as defined in Fig. 1, and $\vec{V}$ is the relative velocity vector between protons. A positive (negative) sign in the exponential corresponds to the electron moving with nucleus $B(A)$. The type of function shown in Eq. (1) was formulated to make allowance for the motion of each nucleus relative to the center of mass of the nuclei (c. m. n.) and is exact for any R when $V = 0$ or for any V when $R = \infty$. The type of velocity dependence suggested by Bates and McCarroll[7] has been widely used[1-4] and has been shown to shift the predicted results toward better agreement with experiment. Performance of calculations with an extended basis made up of orbitals of the type shown in Eq. (1) is, however, made difficult by their strong lack of orthogonality. Thorson[8] has pointed out that this condition is caused by the necessity, in this basis, for the recognition of an electron as "belonging" at all times to one or the other of the colliding centers and moving with the full velocity of that center. In reality, however, during the interaction phase of a slow encounter the electron actually "belongs" to neither. The functions shown in Eq. (1) also display anomalous behavior in the united atom region. Here the electron effectively "sees" a point nucleus with a rapidly changing, albeit negligible, quadrupole moment. Instead of reducing to this, the velocity-dependent factors in Eq. (1) give rise to aphysical sine and cosine terms. Previous authors[9] have, for the most part, attempted to get around the above difficulties by artificially removing the contributions due to nonorthogonality. One of our objectives in this work is to attack the problem at its source by proposing a modified form of basis function which is orthonormal to its partners, is exact in both the separated and united-atom limits, and is devoid of the aphysical aspects of "belonging to" inherent in Eq. (1).

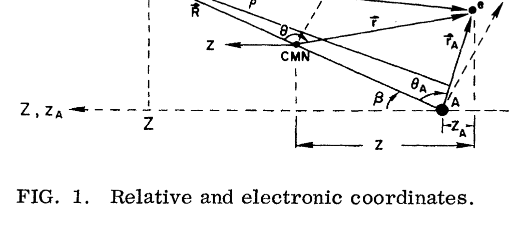

FIG. 1. Relative and electronic coordinates.

The second of the difficulties mentioned above, the reluctance of electronic eigenfunctions to follow the rotation of an internuclear line, was first identified by Bates.[10] Bates found that in the limit of high velocity and weak interaction the two-state version of the pss method did not tend, as it should, to the Born approximation, but tended, instead, incorrectly, to an approximation which he christened the perturbed rotating atom (pra). The two approximations differed in that in the Born approximation, expansion was in terms of orbitals quantized in space-fixed axes, while in the pra approximation quantization was in terms of axes rotating with the internuclear line. Bates[10] found that the pra results could be made to harmonize with the Born approximation if allowance were made for certain terms, previously ignored, which induced strong coupling between states differing in the separated- or united-atom limits in magnetic quantum number only. He also found that this equivalence could be established, *a priori*, by using electronic eigenfunctions quantized in a fixed coordinate system with its z axis parallel to the internuclear velocity $\vec{V}$. Now the entire question is not of great importance as long as an atomic basis set about a single center can be employed. Simply by including all magnetic substates of each atomic state used in the basis set, the rotating and nonrotating basis sets become completely equivalent. However, the picture changes when the physics of the situation requires that a molecular basis set be used instead of an atomic basis set. Although the effect described by Bates still persists, it is not so easy to eliminate in this case, because an infinite number of molecular orbitals is required to make rotating and nonrotating bases equivalent. Since practical considerations permit only a very small number of basis elements to be handled in a computation, it is imperative, therefore, to select the basis elements with care. In a very real sense, the selection of the basis elements used constitutes the definition of the model. Most authors,[2,4,11] in calculations of excitation and charge transfer probabilities, have used orbital bases quantized in a rotating frame in the hope that, by including coupling terms previously omitted, a small number of rotating orbitals would be sufficient. The evidence, however, seems to indicate this is not always the case and that whereas inclusion of terms coupling a limited number of low-lying states may give satisfactory results for transfer of charge between spherically symmetric states,[4] such early truncation may predict side effects, such as excitation, which are highly misleading.[2,4] A second goal of this investigation was, therefore, to present further evidence favoring the use of nonrotating orbitals as a compromise basis which retains some of the molecular orbital characteristics without the aphysical effects of the rotating frame of reference.

II. CRITERIA FOR VELOCITY-DEPENDENT ELECTRONIC FUNCTIONS

It is instructive at this point to enumerate those boundary conditions which should be satisfied by an orbital basis for use in a collision problem. As Bates and McCarroll[7] and Thorson[8] have pointed out, in the limit of infinite internuclear separation each molecular orbital should approach combinations of the corresponding degenerate atomic eigenfunctions which, in the c. m. n. system of relative coordinates and with the electron, for example, on atom A take the form

$$\Phi_n(\vec{r}_A, t) = \chi_n(\vec{r}_A) e^{-im\vec{V}\cdot\vec{r}/2\hbar} \times \exp\{-(i/\hbar)[\epsilon_n + \tfrac{1}{2}m(V/2)^2]t\}. \quad (2)$$

The coordinates in Eq. (2) are as in Fig. 1; $\chi_n(\vec{r}_A)$ and ϵ_n are the nth atomic eigenfunction and eigenvalue, respectively, and the velocity-dependent factor in the wave function and term in the energy appear due to the motion of atom A relative to the c. m. n. The quantity m actually represents a reduced electron mass, but this effect is small. Implicit in Eq. (2) is the requirement that the expectation value of the molecular Hamiltonian also approach the bracketed energy term as $R \to \infty$. The Bates-McCarroll[7]-type wave functions shown in Eq. (1) do satisfy the requirements imposed by the initial and final boundary conditions and do, thereby, take account of transfer of the momentum of the electron in charge exchange. The use of different signs before the exponent $im\vec{V}\cdot\vec{r}/2\hbar$, however, precludes their forming an orthonormal set and is directly related to the very real physical difficulties associated with the requirement for the electron, in this description, to "belong" at all times to one or the other of the interacting atoms. Clearly, a desirable alternative basis would be one composed of orbitals which also matched the asymptotic conditions but which did form an orthonormal set and did allow for the electron to, at times, belong to neither atom.

The form assumed by the wave function in the united-atom limit is also of importance. This point is most easily seen by considering for a moment the wave function for the entire system. It may, at any time, be expanded in terms of products of molecular electronic eigenfunctions $\Phi_n(\vec{r}, \vec{R}(t))$ and purely nuclear components $F_n(\vec{R}(t))$, i.e.,

$$\psi(\vec{r}, \vec{R}(t)) = \sum_n \Phi_n(\vec{r}, \vec{R}(t)) F_n(\vec{R}(t)). \quad (3)$$

This expansion, suggested by Born[12] as a modification to the original Born-Oppenheimer approximation, results in a set of coupled differential equations rigorously relating nuclear and electronic motion. We know, however, that as the united-atom limit is approached, our problem approaches the two-body case of an electron with reduced mass moving with respect to the c. m. n. and that, in this limit, a separation of variables becomes possible and the expansion in Eq. (3) should reduce to a single term wherein the electronic component contains no explicit velocity dependence. This can, in fact, be regarded as the recognition, mathematically, of the physical principle that in this limit for slow collisions the electron "belongs" no more to one nucleus than to the other. Our electronic wave functions and energies which are required to take on the velocity-dependent forms shown in Eq. (2) in the asymptotic region, should gradually lose this dependence as $R \to 0$. The Bates and McCarroll[7] functions in Eq. (1) clearly do not show this behavior; they tend in fact toward real and imaginary velocity-dependent trigonometric functions multiplying the lowest-lying g and u states of the united atom.

Further examination of the system wave function in the united-atom limit reveals still more conditions which should be satisfied by the electronic functions. Substitution of the expansion Eq. (3) into the Schrödinger equation for the system reveals that nuclear and electronic motion are related in such a way that the gradients of the electronic functions with respect to heavy-particle coordinates contribute directly to an effective internuclear potential.[12] Thus the velocity dependence associated with the internuclear potential will be influenced by the type of velocity dependence selected for the Φ_n. By taking the gradient with respect to nuclear coordinates of the effective potential, we can calculate an effective internuclear force. Clearly, if we want the effects associated with the inclusion of velocity dependence to diminish as the united-atom limit is approached, we do not want the effective force terms which are present only because of its inclusion to become dominant as $R \to 0$. Hence we should also require that the derivatives upon which these terms are based become small in the united-atom region. A similar but less powerful argument can be made based upon the appearance of the $\partial/\partial Z$ operator in the matrix elements

$$T^{\pm}_{nm} = \langle \Phi^{\pm}_n | H_{el} - i\hbar V \frac{\partial}{\partial Z} | \Phi^{\pm}_m \rangle, \quad (4)$$

which figure prominently in calculations based on the impact-parameter version of the pss theory.[7]

III. ORTHONORMAL VELOCITY-DEPENDENT ORBITALS

The arguments cited above suggest orbitals of the form

$$\Phi_n^{\pm}(\vec{r},t)=\chi_n^{\pm}(\vec{r},\vec{R})\exp[i(m/2\hbar)\vec{V}\cdot\vec{r}f(\vec{r},\vec{R})]$$

$$\times\exp[-(i/\hbar)\int H_{nn}^{\pm}(t)dt] \qquad (5)$$

for use in a velocity-dependent molecular basis. The functions $\chi_n^{\pm}$ are, for now, to be considered as approximations to the static molecular eigenstates. Complications introduced by the use of a nonrotating basis are discussed in the next section. In any case, the $\chi_n^{\pm}$ are presumed to contain variable orbital exponents so that they can match identically the correct asymptotic and united-atom forms of the adiabatic electronic eigenfunctions. The function $f(\vec{r},\vec{R})$ is introduced in order to insure that the functions $\Phi_n^{\pm}$ match the correct dynamic forms in the separated and united-atom limits without sacrificing the desired condition of orthonormality. With the single universal form of the velocity-dependent exponential in Eq. (5), it is seen that orthonormality of the adiabatic orbitals implies orthonormality of the dynamic orbitals, i.e.,

$$\langle\Phi_n^{\pm}|\Phi_m^{\pm}\rangle=\delta_{nm},\quad \text{if } \langle\chi_n^{\pm}|\chi_m^{\pm}\rangle=\delta_{nm}. \qquad (6)$$

Further, the spatial components of the functions $\Phi_n^{\pm}$ assume the correct limiting forms, provided that functions $f(\vec{r},\vec{R})$ can be found which take on the values +1 (−1) when the electron is on nucleus $B(A)$ in the asymptotic region, and which vanish in the united-atom region. The requirement of vanishing velocity-dependent effective nuclear force terms requires that derivatives of $f(\vec{r},\vec{R})$ with respect to nuclear coordinates also vanish in the united-atom limit. The final factor in Eq. (5) introduces the explicit time dependence of the wave function in a manner analogous to that first proposed by Jeffreys[6,13] for systems with time-dependent but slowly varying Hamiltonians. The terms $H_{nn}^{\pm}(t)$ are not the static energies, but are actual expectation values of the electronic Hamiltonian,

$$H_{nn}^{\pm}(t)=\langle\Phi_n^{\pm}(\vec{r},t)|H_{e1}|\Phi_n^{\pm}(\vec{r},t)\rangle. \qquad (7)$$

They are time-dependent due both to changes in internuclear separation and to changes in the degree of the electron's "belonging" to one atom or another. Evaluated explicitly with the functions shown in Eq. (5), the $H_{nn}^{\pm}$ take the form

$$H_{nn}^{\pm}(t)=\epsilon_n^{\pm}(R(t))$$

$$+(\hbar^2/2m)\int|\chi_n^{\pm}|^2[\vec{\nabla}_r(m\vec{V}\cdot\vec{r}f)/2\hbar]^2d\tau. \qquad (8a)$$

Here $\epsilon_n^{\pm}(R(t))$ is the static electronic energy,

$$\epsilon_n^{\pm}(R(t))=\langle\chi_n^{\pm}(\vec{r},\vec{R})|H_{e1}|\chi_n^{\pm}(\vec{r},\vec{R})\rangle, \qquad (9)$$

and the second term in Eq. (8a) is, at any instant t, just the correction to the electronic energy due to the translational motion impressed on the electron by the dynamical correction factor exp $(im\vec{V}\cdot\vec{r}f/2\hbar)$. The physical significance of this correction factor becomes more transparent if we denote by $U(\vec{r},\vec{R})$ the quantity $\vec{V}\cdot\vec{r}f(\vec{r},\vec{R})/2$, so that the first exponential in the wave function defined by Eq. (5) becomes

$$\exp[im\vec{V}\cdot\vec{r}f(\vec{r},\vec{R})/2\hbar]=\exp[imU(\vec{r},\vec{R})/\hbar].$$

The quantity $\vec{\nabla}_r U$ can be interpreted as the *local* impressed translational velocity. [Note that for the Bates and McCarroll wave function, Eq. (1), this quantity is always $\pm\vec{V}/2$.] Equation (8a) now takes the form

$$H_{nn}^{\pm}(t)=\epsilon_n^{\pm}(R(t))+\tfrac{1}{2}m\int|\chi_n^{\pm}|^2[\vec{\nabla}_r U]^2d\tau. \qquad (8b)$$

The second term is seen to be the local impressed kinetic energy $\frac{1}{2}m[\vec{\nabla}_{\vec{r}}U]^2$ at position $\vec{r}$, weighted by the probability density $|\chi|^2$ that the electron will be at the location $\vec{r}$ and integrated over all space. It is, therefore, the average impressed kinetic energy. From what has already been said, it is clear that in order for $H_{nn}^{\pm}(t)$ to take on the correct limiting forms this term should vanish in the united-atom region and should approach $\frac{1}{2}m(V/2)^2$ as the internuclear separation is increased. Physical reality requires also that this transition be a smooth one.

The conditions imposed upon the function $f(\vec{r},\vec{R})$ by the criteria discussed above are summarized in Table I.

IV. ONE FORM FOR THE FUNCTION $f(\vec{r},\vec{R})$

The function $\cos\theta/[1+(a/R)^2]$ is proposed as suitable for the function $f(\vec{r},\vec{R})$. The angle θ is here measured from the internuclear axis to the position of the electron (Fig. 1) and the quantity a is to be regarded as a relatively small distance below which the electron essentially "sees" a united atom and ceases to "belong" to either nucleus individually. Comparison of the properties of this function with the requirements outlined in Table I shows that the two are in good agreement.

TABLE I. Required behavior for the function $f(\vec{r}, \vec{R})$.

Criterion	Required behavior
1. Orthonormality	f be of same form for all functions Φ_n so that $\langle\chi_n\vert\chi_m\rangle=\delta_{nm}$ implies $\langle\Phi_n\vert\Phi_m\rangle=\delta_{nm}$
2. Asymptotic behavior of wave function	For $r_A \gg r_B$ (large R), $f\rightarrow 1$ For $r_B \gg r_A$ (large R), $f\rightarrow -1$
3. Asymptotic energy correction	As $R\rightarrow\infty$, $[\vec{\nabla}_r(\vec{V}\cdot\vec{r}f)]^2\rightarrow V^2$
4. Intermediate range energy correction	$[\vec{\nabla}_r(\vec{V}\cdot\vec{r}f)]^2$ decrease smoothly with decreasing R
5. United-atom energy correction	As $R\rightarrow 0$, $[\vec{\nabla}_r(\vec{V}\cdot\vec{r}f)]^2\rightarrow 0$
6. United-atom behavior of wave function	As $r_A\rightarrow r_B$ (especially as $R\rightarrow 0$), $f\rightarrow 0$
7. United-atom expression for effective internuclear potential	As $R\rightarrow 0$, $\vec{\nabla}_R f$ and $\vec{\nabla}_R{}^2 f\rightarrow 0$

The first requirement is automatically fulfilled by the choice of the wave function, Eq. (5). A glance at the coordinate system in Fig. 1 reveals that the second requirement is also easily fulfilled. In an Appendix to this paper, we show that requirement No. 2 in Table I is actually not stringent enough. In order for linear combinations of the functions $\Phi_n^{\pm}$ shown in Eq. (5) to exactly match the behavior of the correct asymptotic functions, Eq. (2), not only must $(f\pm 1)\rightarrow 0$ as $R\rightarrow\infty$ (the + sign for the electron on center A, the − sign for the electron on center B), but this quantity must approach zero faster than R^{-1}. With the function suggested here for f, binomial expansion shows that the expressions $(f\pm 1)$ take on the asymptotic forms $2[r_{A(B)}/R]^2\sin^2\theta_{A(B)}$, so that the more stringent form of requirement No. 2 is also met. The term $[\vec{\nabla}_r(\vec{V}\cdot\vec{r}f)]^2$ may be expanded as

$$[\vec{\nabla}_r(\vec{V}\cdot\vec{r}f)]^2=[(\vec{V}\cdot\vec{r})\vec{\nabla}_r f]^2 + 2f(\vec{V}\cdot\vec{r})(\vec{\nabla}_r f\cdot\vec{V})+f^2 . \qquad (10)$$

Examination of the derivatives of $\cos\theta$ reveals that the first two terms on the right-hand side of Eq. (10) vanish as $R\rightarrow\infty$, the third of course approaches unity. Hence, requirement No. 3, the correct form of the asymptotic energy correction, is also met by our proposed function. The trigonometric form of the proposed function and hence, too, of its derivatives insures that requirement No. 4 is also met. Thus the expectation value of the term $[\vec{\nabla}_r(\vec{V}\cdot\vec{r}f)]^2$ varies smoothly from V^2 in the ground state of a separated hydrogen atom to $\frac{7}{15}[1+(a/R)^2]^{-1}V^2$ in the region of the united He$^+$ atom. This last result points up the importance of the factor a. With the distance a set equal to zero, requirement No. 5 could obviously not be met; the energy correction would approach the constant value $\frac{7}{15}[\frac{1}{2}m(V/2)^2]$ in the united-atom limit. However, with a dominating as $R\rightarrow 0$, requirement No. 5 is easily achieved. Requirement No. 6 is satisfied by the geometry of the problem. Finally, we come to requirement No. 7, posed by the physics of an effective internuclear potential. Here again, the requirement is met so long as $(a/R)^2 \gg 1$ as $R\rightarrow 0$. The term $\vec{\nabla}_R f$, for example, blows up as R^{-1} with $a=0$, but vanishes as R^{+1} with nonzero a values. We see then that the use of orbitals of the form shown in Eq. (5) with an f function as suggested above does provide a means for the attainment of a satisfactory orbital basis. The form suggested for the static functions $\chi_n^{\pm}$ is discussed in the next section.

V. NONROTATING ORBTIALS

We have already noted Bates's[10] findings of anomalies in the excitation probabilities predicted by the two-state version of the pss method with the use of molecular-oriented, and hence rotating, orbitals. Mathematically, these difficulties are introduced by the strong coupling between states differing in the separated- or united-atom limits in magnetic quantum number only, caused by the operator $\partial/\partial Z$ in Eq. (4). This is most easily seen when $\partial/\partial Z$ is expressed in terms of rotating coordinates.[10] Physically, the difficulties are caused by the inability of the actual distribution of electronic charge to redistribute itself fast enough to follow rapid rotation of the internuclear line, in short, by a breakdown of the adiabatic approximation. These points are illustrated very clearly by a comparison of the data generated by Bates and Williams[2] with recent unpublished data generated by one of us (A. R.) in conjunction with S. C. Mukherjee. In the discussion which follows, we will follow the guide lines for orbital nomenclature established by Herzberg.[14] Bates and Williams[2] studied the effect of adding H$_2^+$ ($2p\pi$) orbitals to the basis used in calculating charge transfer and excitation probabilities in the H$^+$ on

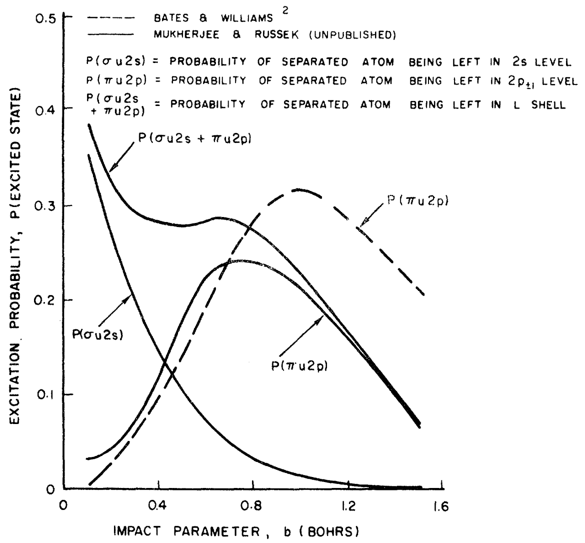

FIG. 2. Excitation probability in the H^+-on-H system, $E = 2$ KeV ($V = 0.283$ a.u.).

H system. This expanded basis gave improved agreement with the experimental charge transfer results,[5] but it was found that the $2p\sigma - 2p\pi$ united-atom coupling terms made the cross section for excitation of the second quantum level remarkably large, and it was concluded that $H_2^+(2p\sigma)$ - $H_2^+(3p\sigma)$ and other couplings might also be of importance. To test this hypothesis, Mukherjee and Russek added the $H_2^+(3p\sigma)$ - $H(\sigma u2s)$ and $H_2^+(4p\sigma)$-$H(\sigma u2p)$ orbitals to the problem and recomputed the excitation probabilities. It was found that while the addition of the highly antibonding $\sigma u2p$ orbital was relatively unimportant, the addition of the $\sigma u2s$ orbital was so important that it significantly changed the excitation probability. In Fig. 2 are shown plots of excitation probability versus impact parameter at an energy of 2 keV as calculated by both sets of authors. The most striking feature of the figure is the following. The Bates and Williams[2] data indicate, as we should expect on physical grounds, that for fixed V, as $b \to 0$, $P \to 0$ (V, relative velocity; b, impact parameter; P, excitation probability). The Mukherjee and Russek data, on the other hand, indicate that when the $\sigma u2s$ state is included in the problem, then although the probability for excitation to a $2p_{\pm 1}$ state still $\to 0$ as $b \to 0$, the probability for excitation to a $2s$ state of the separated atoms continues to increase as b becomes very small, and so also does the total probability for excitation to the L shell. In addition, the Mukherjee and Russek curve for $P(\pi u2p)$, although qualitatively similar to the corresponding Bates and Williams[2] curve, peaks earlier and does not reach as high a maximum.

The reason for the behavior mentioned above becomes clearer from a study of Fig. 3. In Fig. 3 are shown curves for the probability of occupancy of the ground state and the two lowest-lying excited states of ungerade symmetry, plotted for the small impact parameter $b = 0.1$ bohr versus the angle $(\frac{1}{2}\pi - \beta)$, the complement of angle β shown in Fig. 1. Here again there are several things apparent from the figure, but one is most striking. Both the Bates and Williams[2] and the Mukherjee and Russek curves for $P(\pi u2p)$ build steadily until the region near $(\frac{1}{2}\pi - \beta) = 0$ and then trail off again. However, whereas in the Bates and Williams[2] result depletion of the $\pi u2p$ level results automatically in a repletion of the $\sigma u1s$ level, in the Mukherjee and Russek result depletion of the $\pi u2p$ state results mainly in a building of the $\sigma u2s$ state. The effect of the truncation introduced by Bates and Williams[2] in omitting this latter state is seen to be severe. By so doing they obtain, fortuitously, results of the type shown in Fig. 2 which appear to be qualitatively correct. However, as soon as the approximation is carried one step further, the type of behavior exhibited in Fig. 3 which accounts for the weird behavior of the $P(\sigma u2s + \pi u2p)$ curve in Fig. 2, is obtained. The reason for this is not hard to find. From the Bates and Williams[2] data in Fig. 3, it can be seen that in the region near $\beta = \frac{1}{2}\pi$($Z = 0$ in Fig. 1) the wave function becomes essentially all $\pi u2p$, which means that although the internuclear axis has rotated through an angle of $\frac{1}{2}\pi$, the actual orbital wave function describing the electron has, for this small impact parameter, rotated not at all. When the sign of the coefficient weighting the contribution to the total wave function of the $\sigma u1s$ orbital is examined, this result becomes even clearer. Examination of the data indicates that this coefficient starts out at -0.707, passes through zero near $(\frac{1}{2}\pi - \beta) = 0$, and finally returns very close to its initial value, with, however, a change in sign indicating that although the molecule-oriented axis has flipped, the original σ orbital in

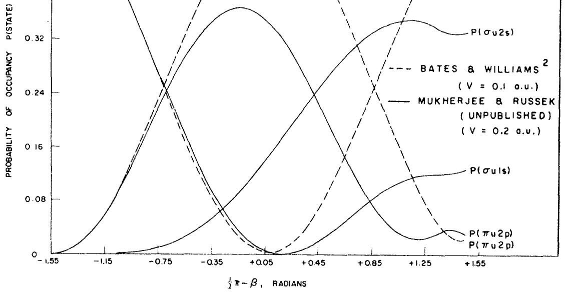

FIG. 3. Excitation probability as a function of angle in the H^+-on-H system, impact parameter $= 0.1$ bohr.

which the electron started out has not. These results are in good agreement with classical intuition. If the electron is considered to perform orbital motion about one of the centers, with angular velocity ω_e of 1 a.u., then it is likely that reluctance of the corresponding eigenfunction to follow rotation of the internuclear line, given by angular velocity ω_N, will begin to appear when $\omega_e \leqslant \omega_N$. Expressing all quantities in a.u., the ratio ω_N/ω_e is given, in general, and at the point of closest approach, in particular, by the first and the second of the following equalities, respectively:

$$\omega_N/\omega_e = (V/R)\sin\beta = V/b\,, \tag{11}$$

where b is the impact parameter, R is the internuclear separation, and β is the angle defined in Fig. 1. For the data plotted in Fig. 3 the "threshold value" $V/b = 1.0$ has been reached, and the reluctance of the electronic functions to follow the nuclear rotation is clear. The data indicate that if the orbital basis is constructed, nevertheless, from functions which do rotate, then the $\pi u2p$ orbital, as it depopulates, selectively fills the $\sigma u2s$ orbital when given the opportunity to do so. That this should happen is really not very surprising, since as the separated atoms limit is approached these two levels become degenerate and each lies some 9.8 eV above the $\sigma u1s$ level. The importance of the $\pi u2p$ - $\sigma u2s$ coupling, while mathematically logical, accounts, however, for the anomalously large probability of excitation indicated in Fig. 2 for small impact parameters. This, in turn, strongly suggests the inadequacy of early truncation when the orbital basis is written in terms of rotating functions and suggests the possible superiority of a nonrotating orbital basis.

These arguments are given further weight by the additional data of Mukherjee and Russek which are shown in Table II. In Table II excitation probabilities P (excited state) are tabulated against impact parameter for a velocity of 0.2 a.u. at values of $(\frac{1}{2}\pi - \beta)$ of 0, $(\frac{1}{2}\pi - \beta)_{\pm 1(\max)}$, and 1.55 rad. The quantity $(\frac{1}{2}\pi - \beta)_{\pm 1(\max)}$ is defined as that angle where $P(\pi u2p)$ reaches a maximum in curves of the type shown in Fig. 3. The other two angles represent the mid and end points of the collision. For each of the angles we list $P(\pi u2p)$ and $P(\sigma u2s)$. The $\sigma u2s$ state is reached from the $\sigma u1s$ state only with the $\pi u2p$ state as an intermediary. Hence the sum $P(\sigma u2s + \pi u2p)$ gives the best indication of the importance of rotational effects at $(\frac{1}{2}\pi - \beta) = 0$ as well, of course, as giving the final probability of excitation at $(\frac{1}{2}\pi - \beta) = 1.55$ rad, and it too is tabulated for these two angles. From Table II we see that at a given V as b is decreased and hence the ratio V/b is increased from considerably below to somewhat above unity, the sum $P(\sigma u2s + \pi u2p)$ evaluated at $(\frac{1}{2}\pi - \beta) = 0$ increase steadily, indicating the increasing reluc-

TABLE II. Excitation probability in the H^+-on-H system at fixed internuclear velocity ($v = 0.2$ a.u.), unpublished data of Mukherjee and Russek.

		$(\frac{1}{2}\pi - \beta) = 1.55$ rad				$(\frac{1}{2}\pi - \beta)_{\pm 1}$ max		$(\frac{1}{2}\pi - \beta) = 0$		
b (bohr)	V/b	$P)\sigma u2s + \pi u2p)$	$P(\sigma u2s)$	$P(\pi u2p)$	$(\frac{1}{2}\pi - \beta)_{\pm 1\,(\max)}$ (rad)	$P(\sigma u2s)$	$P(\pi u2p)$	$P(\pi u2p)$	$P(\sigma u2s)$	$P(\sigma u2s + \pi u2p)$
0.1	2.0	0.3635	0.3325	0.0310	−0.15	0.0907	0.3691	0.3595	0.1258	0.4853
0.25	0.8	0.2695	0.1495	0.0750	−0.025	0.0749	0.3933	0.3931	0.0749	0.4680
0.5	0.4	0.3001	0.0525	0.2476	+0.325	0.0550	0.4136	0.3752	0.0281	0.4033
0.7	0.29	0.2596	0.0159	0.2437	+0.5	0.0294	0.3949	0.3162	0.0122	0.3284
1.0	0.2	0.1823	0.0017	0.1806	+0.5	0.0076	0.3035	0.2277	0.0038	0.2315
1.5	0.13	0.0176	0.0000	0.0176	+0.3	0.0004	0.1004	0.0839	0.0003	0.0842

tance of the electronic wave function to follow the rotation of the internuclear line. We also see from Table II that for small b the maximum in the $P(\pi u2p)$ versus $(\frac{1}{2}\pi-\beta)$ curve is reached earlier, thereby giving it more time to deplete to the $\sigma u2s$ state than for larger impact parameters where this maximum is reached much later in the collision process. For small b, therefore, the final value of $P(\sigma u2s)$ is large and curves of the type shown in Fig. 2 differ markedly from those of Bates and Williams.[2] For large b, however, the maximum in $P(\pi u2p)$, although considerably smaller, is reached much later, has less time to deplete to $\sigma u2s$, and gives a curve in at least qualitative agreement with those of Bates and Williams. This, of course, is consistent with the earlier arguments, since as b increases V/b decreases and so does the reluctance of the electronic functions to rotate. Browne[15] has independently confirmed the results just discussed. The recent results of Gallaher and Wilets[4] and of Cheshire[4] confirm the conclusion that arbitrary early truncation of a basis expressed in terms of rotating orbitals is disallowed by rapid rotation of the internuclear line. The action of the $\partial/\partial Z$ operator couples orbitals of this type which differ, in some region, in magnetic quantum number only; the inclusion of each additional orbital seems to beget the inclusion of another.

The considerations just discussed suggest the use, for the $\chi_n^{\pm}$ appearing in Eq. (5), of linear combination of atomic orbitals–molecular orbitals which are made up of atomic orbitals quantized in the nonrotating (unprimed in Fig. 1) frame. For the lowest state of each symmetry type, these might be expressed, for example, in a simple approximation as

$$\chi_0^{\pm}(\vec{r},\vec{R})=C_s^{\pm}(\vec{R})\{N_s^{\pm}(\vec{R})[e^{-\alpha r_A}\pm e^{-\alpha r_B}]\}$$
$$+C_p^{\pm}(\vec{R})\{N_p^{\pm}(\vec{R})[z_A e^{-\alpha r_A}\mp z_B e^{-\alpha r_B}]\}. \quad (12)$$

The molecular orbitals $\chi_0^{\pm}$ are made up of two contributions, $1s$ and $2p_0$, which are themselves already normalized by the $N_s^{\pm}$ and $N_p^{\pm}$ terms and are quantized along the nonrotating axis. The coefficients $C_s^{\pm}$ and $C_p^{\pm}$ give the respective contributions of the two terms. The exponent α is allowed to vary freely as a function of internuclear separation. Use of this type of orbital amounts to a compromise between the two extremes of (1) the high-velocity case wherein the Born approximation is most appropriate and the expansion is in terms of unperturbed atomic eigenenergies and eigenstates quantized along space-fixed axes, and (2) the very low-velocity case wherein the pss approximation is most appropriate and the expansion is in terms of exact molecular eigenenergies and eigenstates quantized along axes which rotate with the internuclear line (see also Cheshire,[4] in this connection). These orbitals tend to the correct high-velocity limit and are unencumbered by rotation-related difficulties. It turns out, too, that they also provide an approximation to the exact static molecular energies nearly as good as similar functions which do rotate. Calculations of charge transfer probability which are based upon the orbitals in Eqs. (5) and (12) are presented in the next section.

VI. CHARGE TRANSFER IN THE TWO-STATE APPROXIMATION WITH NONROTATING ORBITALS

As a first use of the new type of velocity-dependent and nonrotating orbital forms suggested here, calculations have been performed in the two-state approximation for charge transfer probability in the famous 3° H^+ on H scattering experiments of Everhart *et al.*[5] The expression for $P_B(E)$, the charge transfer probability, is superficially similar in form to that first derived by Bates and McCarroll,[7]

$$P_B(E)=\sin^2\zeta, \quad (13)$$

$$\text{where}\quad \zeta=(2\hbar)^{-1}\int_{-\infty}^{\infty}[T_{00}^{+}-T_{00}^{-}]\,dt. \quad (14)$$

However, in our case the quantities $T_{00}^{\pm}$ are given by

$$T_{00}^{\pm}=H_{00}^{\pm}+\tfrac{1}{2}mV^2\langle\chi_0^{\pm}|z\,\partial f/\partial Z|\chi_0^{\pm}\rangle, \quad (15)$$

with $H_{00}^{\pm}$ as defined in Eq. (8) and coordinates as in Fig. 1. The expressions for $H_{00}^{\pm}$ and $T_{00}^{\pm}$ together with the united-atom behavior imposed earlier upon the function $f(\vec{r},\vec{R})$ reveal, upon closer inspection, that our expression for $P_B(E)$ actually differs considerably from that in Ref. 7. Most noticeably, the trigonometric type integrals, which there enter into the calculation because of the nonorthogonality of the orbitals, are here replaced by integrals which enter due to the variation in f necessary to correctly match all boundary conditions.

Values of the charge transfer probability for 3° scattering were calculated over the range of energies covered by experiment,[5] approximately 1–50 keV. The variable parameters appearing in the adiabatic functions $\chi_0^{\pm}$ were determined by the Rayleigh-Ritz determinantal form of the variation principal[16] through minimization of the adiabatic electronic energies $\epsilon_0^{\pm}$. Both linear and exponential parameters were optimized. All integrations needed in the evaluation of the adiabatic terms were performed analytically, some taken from the work of Rosen[17] and others evaluated explicitly in prolate spheroidal coordinates.[18]

The expectation values of the nonadiabatic terms in $H_{00}^{\pm}$, Eq. (8), are not evaluable in closed form. These integrations were accomplished numerically in prolate spheroidal coordinates. 32-point Lobatto quadrature[19] was used for integration over $\eta(-1 \leq \eta \leq 1)$ and 32-point Laguerre quadrature[20] for integration over $\xi(1 \leq \xi \leq \infty)$. Finally, integration over nuclear coordinates was accomplished by 11-point Lobatto quadrature.[19] These last integrations were carried out to an internuclear separation $Z = 10.0$ a.u. (Fig. 1), at which point the integrand in Eq. (14) was already 2 to 3 orders of magnitude below its maximum value.

The results of the calculations are shown in Table III. Since we have chosen, initially, to perform the calculations in the two-state approximation, there is no damping predicted; its inclusion requires the use of channels of excitation[2] and/or a full wave treatment.[3] We are interested then, in these particular calculations, only in the location of the extrema in the $P_B(E)$ versus E curve, and it is these that are tabulated in Table III. They are tabulated for both the nonrotating orbitals shown in Eqs. (5) and (12) and the similar rotating orbitals which are obtained by replacing $z_{A,B}$ in Eq. (12) by $z''_{A,B}$ (Fig. 1). The data of Ferguson,[1] which were obtained using the rotating orbital approximation for H_2^+ given by Dalgarno and Poots[21] are also shown, as are the experimental data.[5] For each of the theoretical cases the extrema are given both with and without the inclusion of the velocity-dependent correction functions in $H_{00}^{\pm}$ and $T_{00}^{\pm}$. None of the theoretical results are in anywhere near as good agreement with experiment as the very large basis results of Gallaher and Wilets[4] and of Cheshire,[4] but this is to be expected and is not here the point. Comparison of the three columns labeled "a" indicates that for the particular resonant charge-exchange process being studied, orbital orientation is not very important. This is especially true for small impact parameters, where small values of the angle β, i.e., significant rotations of the internuclear line, are not reached until the near united-atom region. For these cases, by the time rotation of the internuclear line is great enough so that, at moderate R, it would effect the calculation of the $T_{00}^{\pm}$ terms, the actual R is already small enough so that what is being calculated is, in effect, a perturbed atomic energy which is independent of rotation of orbitals. This insignificance, here, of orbital orientation is not very surprising when one considers that by limiting ourselves in these first calculations to the two-state approximation, we have restricted ourselves to initial and final states that are all spherically symmetrical, thereby automatically excluding the anomolous coupling effects of the $\partial/\partial Z$ operator on rotating orbitals. Our previous discussion of Fig. 3, and the work of Bates,[10] Gallaher and Wilets,[4] and Cheshire,[4] makes it clear that the salient feature of the use of nonrotating orbitals, the elimination of this anomoly, will appear only when the basis is expanded sufficiently to include a study of excitation effects as well.

The good agreement exhibited in Table III between the results of Ferguson[1] and the current results for the adiabatic case makes possible a comparison of the effect of the velocity-dependent correction suggested by Bates and McCarroll,[7] Eq. (1), and the type suggested here, Eq. (5). From Eqs. (8), (14), and (15) it is clear that the nonadiabatic phase corrections to the charge transfer probability are proportional to V. Hence as would be expected, the data in Table III indicate these corrections are negligible at the lowest energies considered, $E \approx 1$ keV. For energies much above 25 keV, which corresponds to a proton velocity of 1 a.u., the whole concept of a perturbed stationary state becomes invalid. One would expect, therefore, that the most meaningful area for the type of nonadiabatic correction suggested here would be at or near the 25-keV mark. The data in Table III indicate that this is the case. The corrected extrema calculated with the f function corrections become progressively better as E is increased to near this limit. Additional data show that beyond this point the corrections tend to over-shift, i.e., to place the next extremum below the experimental value. With the Bates-

TABLE III. Results of charge transfer calculations in the two-state approximation for 3° scattering in the H^+-on-H system; a, without velocity-dependent corrections; b, with velocity-dependent corrections.

	Ferguson (Ref. 1)		Rotating orbitals		Nonrotating orbitals		
Extrema	a	b	a	b	a	b	Experiment (Ref. 5)
max	58.4	16.9	•••	•••	58.4	21	21
min	14.6	6.95	•••	•••	15.0	10	7.8
max	6.48	4.06	6.5	5.2	6.5	5.4	3.9
min	3.65	2.70	3.7	3.2	3.7	3.3	2.4
max	2.34	1.96	2.3	2.1	2.3	2.2	1.6
min	1.63	1.51	1.5	1.4	1.5	1.4	1.1
max	1.19	•••	1.0	1.0	1.0	1.0	0.78

McCarroll[7]-type function this overshift occurs at much lower energies and so, consequently, does the area of best agreement with experiment.

A final determination of the practical merits of the new type of velocity dependence suggested in Eq. (5) must await the performance of more detailed calculations. For one thing, we have in these preliminary calculations optimized the orbital wave functions with respect to the static electronic energies $\epsilon_0^\pm$. A better procedure would be to fully optimize these functions with respect to the actual expectation value $H_{00}^\pm$ shown in Eq. (8). And, as pointed out by Mittleman[9] and developed by Cheshire,[4] a still better procedure, which fully takes account of the dynamic nature of the encounter, is to minimize the integral

$$I_n^\pm = \int_{-\infty}^{\infty} \langle \Phi_n^\pm \,|H_{e1} - i\,\partial/\partial t\,|\Phi_n^\pm\rangle\, dt. \tag{16}$$

The integral in Eq. (16) will, of course, vary with impact parameter b. Use of the variation principle in its minimization will therefore be more powerful if the parameter "a" appearing in $f = \cos\theta/[1+(a/R)^2]$ is allowed to vary with b. As mentioned earlier, this parameter is to be regarded as a relatively small distance below which the electron essentially "sees" a united atom and ceases to belong to either nucleus individually. That "a" should vary with the relative velocity V, and hence, for fixed angle scattering, with the impact parameter b, is therefore entirely consistent with and even required by its physical interpretation. In the calculations performed thus far, "a" was regarded as constant for an entire $P_B(E)$ versus E curve, and it was found that the best values of the charge-exchange probability, those given in Table III, were obtained with "a" values of the order of $\frac{1}{8}$ to $\frac{1}{16}$ a.u. For smaller "a" values, derivatives of the f function blow up and the correct united-atom behavior is not achieved; for larger "a" values, the velocity-dependent terms are damped out too quickly and the correction terms calculated are too small. Further investigations into the best form for the f function and the effect of nonrotating orbitals on excitation probability are required.

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APPENDIX

Asymptotic Form of the Wave Function

In the impact-parameter version of the method of pss, the time-dependent wave function describing the electronic state of the system is expanded as

$$\Phi(\vec{r}, t) = \sum_n C_n^\pm(t)\,\Phi_n^\pm(\vec{r}, t). \tag{17}$$

The form of the $\Phi_n^\pm(\vec{r}, t)$ suggested here are shown in Eq. (5). The static part of the $\Phi_n^\pm(\vec{r}, t)$, the $\chi_n^\pm(\vec{r}, \vec{R})$ shown in Eq. (12), display the usual asymptotic behavior, namely,

$$2^{-1/2}[\chi_0^+(\vec{r}, \vec{R})\,(\pm)\,\chi_0^-(\vec{r}, \vec{R})]$$
$$\to \chi_0(\vec{r}_{A(B)}), \text{ as } R \to \infty. \tag{18}$$

Derivation of the expression, Eq. (13), for the probability of capture by proton B of an electron initially on atom A requires a knowledge of the coefficients $C_0^\pm(-\infty)$ weighing, in Eq. (17), the contribution of the $\Phi_0^\pm(\vec{r}, t)$ to the wave function describing the initial electronic state of the system. This latter is given by Eq. (2) with $n = 0$. Substituting Eq. (18) into Eq. (2) and the resultant into Eq. (17) gives, upon inner product formation with the $\Phi_0^\pm$ of Eq. (5),

$$C_0^\pm(-\infty) = 2^{-1/2}\int d\tau\, |\chi_0^\pm|^2$$
$$\times \exp\{-(im/2\hbar)\vec{V}\cdot\vec{r}\,[1 + f(\vec{r}, \vec{R})]\}. \tag{19}$$

In obtaining Eq. (19) we have made use of requirement (3) in Table I. In order for combinations of the $\Phi_0^\pm$ to behave as asymptotically exact wave functions, the integral in Eq. (19) should approach unity as $R \to \infty$. Using Eqs. (18) to transform to atomic eigenfunctions and expanding the exponential, Eq. (19) may be rewritten as

$$C_0^\pm(-\infty) = 2^{-1/2}\int d\tau\, |\chi_0(\vec{r}_A)|^2$$
$$\times \sum_{n=0}^{\infty} \frac{1}{n!}\left(-im/2\hbar\vec{V}\cdot\vec{r}\,[1 + f(\vec{r}, \vec{R})]\right)^n. \tag{20}$$

A study of Fig. 1 reveals the following trigonometric equality:

$$\vec{V}\cdot\vec{r} = Vz = V(z_A - \tfrac{1}{2}R\cos\beta). \tag{21}$$

With the electron on A, $\cos\beta = -1$. The $\vec{V}\cdot\vec{r}$ term in Eq. (20) therefore contains a term linear in R which can cancel exactly any R^{-1} dependence appearing in the asymptotic form of $(1+f)$ when the multiplication indicated in Eq. (20) is performed. The series form of the exponential makes it clear that the expectation value of the quantity in brackets will consequently vanish as $R \to \infty$ only for functions $f(\vec{r}, \vec{R})$ for which the quantity $(1+f) \to 0$, as $R \to \infty$, faster than R^{-1}. For functions which do meet this criterion such as, for example, $\cos\theta$, the integral in Eq. (19) does approach unity as $R \to \infty$ and the wave functions are asymptotically exact.

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