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Pion molecular orbitals

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The formation of pion molecular orbitals is investigated theoretically for an isolated system consisting of a pion and two nuclei whose separation corresponds to typical molecular bond lengths. The validity of the Born-Oppenheimer approximation is investigated and confirmed. The effect, not previously studied, of the electrons which are associated with the chemical bond between the pair of nuclei in a molecule has been examined. Although it is standard practice to neglect the effect of the molecular electrons on the captured pion, except possibly for a constant screening factor, we find that this effect is of major importance. In particular, this effect illuminates the process in which a pion, initially captured in hydrogen, is transferred to a neighboring heavier atom.

I. INTRODUCTION

Many experiments at the Joint Institute for Nuclear Research (Dubna), Organisation Européenne pour la Recherche Nucleáire (CERN), Schweizerisches Institut für Nuklearforschung (SIN), and TRIUMF have shown that pion and muon interactions with matter are sensitive to molecular structure.[1] These data have been interpreted through various versions of the mesomolecular model.[2-6] This model postulates that a pion may be captured directly into an atomic orbital or it may first be captured into a molecular orbital and then subsequently be captured by one of the atoms of the molecule.

There is general agreement that pions initially captured by hydrogen have a low probability of cascading through the hydrogenic states and ultimately interacting with the proton through the nuclear interaction because of a competing "transfer" process. In the model developed by Ponomarev and co-workers, as applied to gas mixtures, it is assumed that the small neutral $p\pi^-$ system diffuses through the material until it collides with a heavier atom and the pion is transferred to this atom.[2-4] In the model developed by Jackson and co-workers[6,7] for capture in molecules, transfer is assumed to take place to the nearest-neighboring atom, which is the one to which the hydrogen is bonded, and the mechanism is pictured as a tunneling process.

The purpose of this work is to investigate theoretically the formation of pion molecular orbitals for an isolated system consisting of a pion and two fixed nuclei whose separation corresponds to typical molecular bond lengths. The standard method of calculation involves the use of the Born-Oppenheimer approximation but, in this case, it is necessary to justify the validity of this approximation because of the increased mass of the pion compared with the electron. These calculations for bare nuclei are reported in Sec. II. In Sec. III we consider the effect, not previously studied, of the electrons which are associated with the chemical bond between any pair of nuclei in a molecule. It turns out that this effect is significant and, in particular, illuminates the interpretation of hydrogen transfer.

II. THE TWO-CENTER SYSTEM WITHOUT ELECTRONS

A. Units of length and energy

The units used for length a_π and energy W_π are known as mesoatomic units, with $m_\pi=\hbar=e=1$. In terms of the electronic Bohr radius a_e (0.529 Å) and a standard energy E_1 taken to be 27.2 eV, these mesoatomic units are given by

$$a_\pi=a_e m_e/M_\pi \tag{1}$$

and

$$W_\pi=E_1 M_\pi/m_e\ , \tag{2}$$

where

$$M_\pi=\frac{m_\pi(m_p n_p+m_n n_n)}{m_\pi+m_p m_p+m_n n_n} \tag{3}$$

is the reduced mass of the complete system; m_p, m_n, and m_π are the proton, neutron, and pion masses, respectively; and n_p and n_n are the total number of protons and neutrons for the two centers.

Values of a_π and W_π are tabulated in Table I for different combinations of atoms of atomic number Z_1 and Z_2 of interest in this work. 1 Å is a typical bond length between these centers in many molecules. This length corresponds to approximately $500a_\pi$, which is taken as the center separation for many of the calculations to follow.

TABLE I. Values of a_π and W_π for different centers.

Z_1	Z_2	a_π (10^{-15} m)	W_π (keV)
1	1	208.1	6.915
6	1	196.0	7.345
7	1	195.7	7.357
8	1	195.4	7.365
8	6	194.7	7.390

B. The Schrödinger equation for the two-center system

The Schrödinger wave equation for a two-center system is given in mesoatomic units by[8]

$$\left[-\frac{\nabla_R^2}{2M} - \frac{\nabla_\pi^2}{2} + V(\mathbf{R},\mathbf{r}_\pi) \right] \psi_i(\mathbf{R},\mathbf{r}_\pi) = \epsilon \psi_i(\mathbf{R},\mathbf{r}_\pi) \; , \quad (4)$$

where ∇_R^2 is the kinetic-energy operator for the center of mass of the two nuclei, ∇_π^2 is the kinetic-energy operator for the pion, $V(\mathbf{R},\mathbf{r}_\pi)$ is the sum of all electrostatic interactions.

$$\begin{aligned} V(\mathbf{R},\mathbf{r}_\pi) &= V(\mathbf{r}_\pi) + Z_1 Z_2 / R \\ &= -Z_1/r_1 - Z_2/r_2 + Z_1 Z_2 / R \; , \end{aligned} \quad (5)$$

r_1 and r_2 and the distances for the pion from Z_1 and Z_2, respectively, R is the internuclear separation, and ϵ is the total energy of the system.

C. The Born-Oppenheimer approximation

The Born-Oppenheimer approximation[9] states that the nuclear motion and the pion motion can be separated and that the potential energy of the pion in the field of the two nuclei can be used to describe the nuclear motion. Thus (dropping the subscript i) $\psi(\mathbf{R},\mathbf{r}_\pi)$ can be rewritten as

$$\psi(\mathbf{R},\mathbf{r}_\pi) = u(\mathbf{R};\mathbf{r}_\pi) v(\mathbf{R}) \; , \quad (6)$$

where $u(\mathbf{R};\mathbf{r}_\pi)$ is the pion wave function with the nuclei fixed at an internuclear separation $\mathbf{R}$, and $v(\mathbf{R})$ is the wave function for the nuclear motion. If (6) is substituted in (4), then

$$\begin{aligned} &\left[-\frac{\nabla_R^2}{2M} - \frac{\nabla_\pi^2}{2} + V(\mathbf{R},\mathbf{r}_\pi) \right] u(\mathbf{R};\mathbf{r}_\pi) V(\mathbf{R}) \\ &\quad = \epsilon u(\mathbf{R};\mathbf{r}_\pi) v(\mathbf{R}) - \frac{1}{2M} \left[2 \frac{\partial u}{\partial R} \frac{\partial v}{\partial R} + \frac{\partial^2 u}{\partial R^2} v \right] . \end{aligned} \quad (7)$$

The accuracy of the Born-Oppenheimer approximation therefore depends on the magnitude of the extra term,

$$-\frac{1}{2M} \left[2 \frac{\partial u}{\partial R} \frac{\partial v}{\partial R} + \frac{\partial^2 u}{\partial R^2} v \right] ,$$

when compared to the kinetic energy of the nuclei, $P_n^2/2M$ (P_n is the momentum of the center of mass of the nuclei and M is the reduced mass of the two nuclei). The standard discussion[8] leads to the condition

$$(m_\pi / M)^{1/4} \ll 1 \; . \quad (8)$$

For electrons this condition is satisfied by virtue of the large mass difference between the electron and the nuclei. The approximation is inevitably less accurate for pions, especially for systems with nuclei of low mass.

D. The pion potential

Assuming, at this stage, that the Born-Oppenheimer approximation is valid for pions, the Schrödinger equation can be rewritten as

$$[-\tfrac{1}{2} \nabla_\pi^2 + V(\mathbf{R},\mathbf{r}_\pi)] u(\mathbf{R},\mathbf{r}_\pi) = E(R) u(\mathbf{R};\mathbf{r}_\pi) \; , \quad (9)$$

which is identical to the original wave equation, except that the kinetic-energy operator of the nuclei is omitted. $E(R)$ is the energy of the pion and includes the nuclear repulsion energy $Z_1 Z_2 / R$. The purely pionic energy is given by a similar Schrödinger wave equation,

$$\left[-\frac{\nabla_\pi^2}{2} + V(\mathbf{r}_\pi) \right] u(\mathbf{R};\mathbf{r}_\pi) = W(R) u(\mathbf{R};\mathbf{r}_\pi) \; , \quad (10)$$

with $W(R) = E(R) - Z_1 Z_2 / R$. $V(\mathbf{r}_\pi)$ is the potential field in which the pion moves and will determine the nature of the potential barrier between the two centers. The function $E(R)$ can be used as the potential-energy function to obtain the wave function for the nuclear motion from

$$\left[-\frac{\nabla_R^2}{2M} + E(R) \right] v(\mathbf{R}) = \epsilon v(\mathbf{R}) \; . \quad (11)$$

The shape and height of the barrier are very important, as they will govern the formation of molecular orbitals. In the mesomolecular models which ignore the possibility of tunneling[2-4] it is assumed that there is a sharp transition between atomic states below the barrier and molecular states which can exist only within the energy range between the height of the potential barrier and the zero of energy.

Contour plots of $V(\mathbf{r}_\pi)$ in the y-z plane and $V(\mathbf{r}_\pi)$ along the internuclear axis (z axis) are presented in Fig. 1 for H—H, C—H, N—H, O—H, and O—C bonds. The internuclear separations for these bonds were obtained from the molecules of hydrogen (H_2), methane (CH_4), ammonia (NH_3), water (H_2O), and carbon dioxide (CO_2). In order to compare with similar bonds in different molecules, C—H and O—H bonds were also examined in methanol (CH_3OH) and the N—H bond was examined in hydrazine (N_2H_4). Henceforth, the first group of molecules will be referred to as group-A molecules and the second group as group-B molecules. The bond lengths are given in Table II. The small differences in $V(\mathbf{r}_\pi)$ between group-A and group-B molecules are not evident on the scale of Fig. 1.

The value of the principal quantum number which corresponds to the atomic energy state nearest to the height of the barrier separating the two potential wells in $V(r_\pi)$ is given by[10]

$$n_0(Z_1) = \left[\frac{Z_1 R}{2[1 + 2(Z_2/Z_1)^{1/2}]} \right]^{1/2} . \quad (12)$$

(This formula is given incorrectly in Refs. 3 and 4.) The values of $n_0(Z_1)$ and $n_0(Z_2)$ are given in Table II. States with $N \leq n_0$ in either atom are regarded[2-4] as atomic states, while those states above the barrier are regarded as molecular states. It can be seen from Fig. 1 that the barrier is sufficiently low to allow the formation of molecular states.

E. United atom and separated atom quantum numbers

The quantum numbers most commonly used to label a molecular state are the united atom quantum numbers

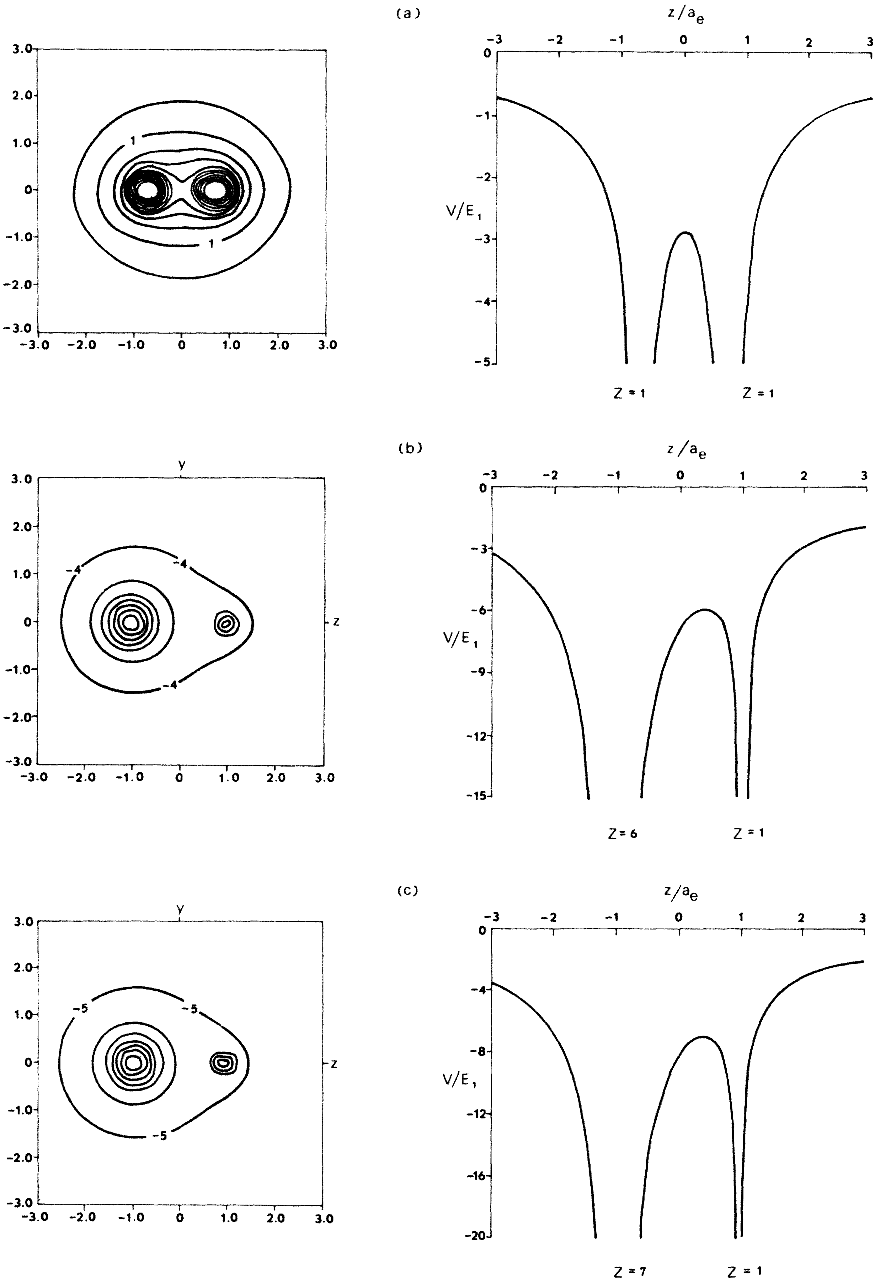

FIG. 1. Plots of $V(\mathbf{r}_\pi)$, in units of E_1, for the two-center systems derived from group-A molecules: (a) H—H, (b) C—H, (c) N—H, (d) O—H, (e) O—C.

(n,l,m). These refer to the limit of $R=0$ where the two nuclei combine to form a single nucleus of charge $Z=Z_1+Z_2$. The principal quantum number n runs over the positive integers $n=1,2,3,4,\ldots$ and the angular momentum quantum number l takes the usual values $l=0,1,2,3,\ldots,n-1$ corresponding to $s,p,d,f,\ldots$, etc., states. The energy curves of the pion energy $W(R)$ will converge to values of $\frac{1}{2}(Z/n)^2$ at $R=0$. m is the quantum number which measures the component of angular momentum along the axis of the molecule and takes the values $m=0, \pm1, \pm2, \pm3, \pm4, \ldots, \pm l$ with doubly degenerate levels for $\pm m$ except for $m=0$. States with $m=0$ are referred to as σ states, those with $m=\pm1$ as π states, those with $m=\pm2$ as δ states, etc. For homonuclear two-center systems, the states are also denoted by a subscript g for even (gerade) states and u for odd (ungerade) states. The parity of the state is determined by whether the wave function changes sign or not after inversion in the midpoint between the nuclei.

It is also possible to use separated atom quantum numbers (N,K,m) to define a particular quantum state. These quantum numbers are obtained by separating the two centers to infinity ($R=\infty$), where the energy curves tend to atomic states around Z_1 and Z_2, with energies of

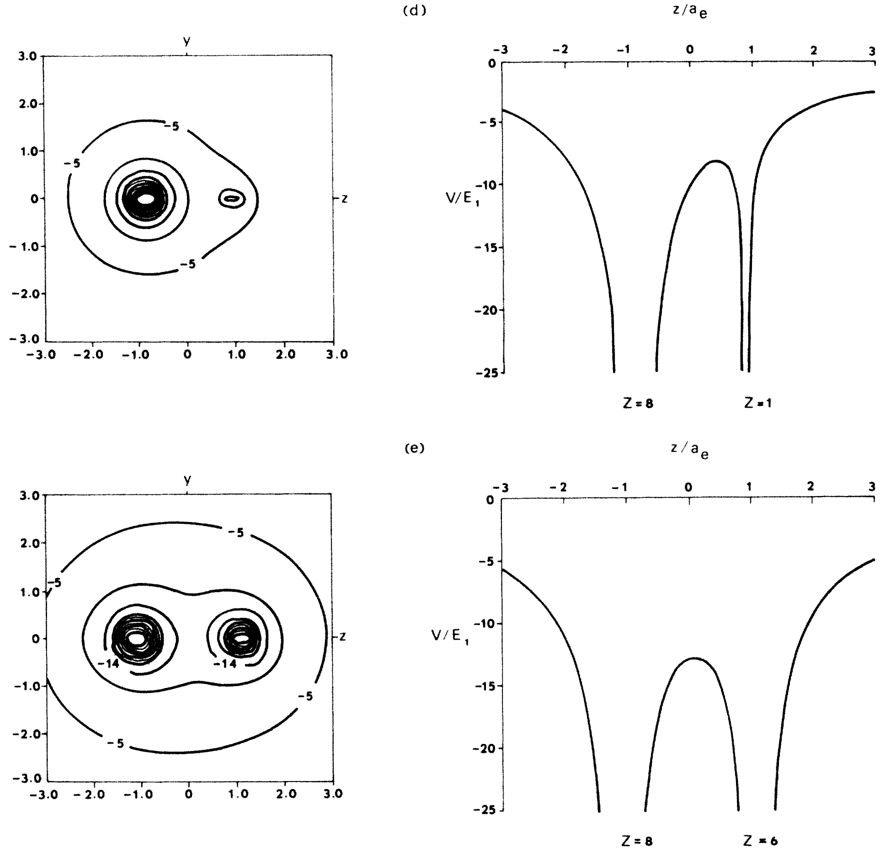

FIG. 1. (*Continued*).

$\frac{1}{2}(Z_1/N_1)^2$ and $\frac{1}{2}(Z_2/N_2)^2$, respectively. N and K are related to the united atom quantum numbers by the correlation[11]

$$N=n-l+m+K\ ,$$
$$K=[l+m]/2\ , \tag{13}$$

where $[x]$ is the integer part of x for the homonuclear case and by a more complicated correlation for the heteronuclear case. The m quantum number is identical to that of the united atom quantum numbers. Values of n_0 tabulated in Table II refer to the separated atom principal quantum numbers for each of the two centers.

F. The solution of the Schrödinger equation

The solution of the Schrödinger equation[9] can be found by the introduction of confocal elliptic coordinates which allows the wave function to be written as[12–14]

$$\psi(\mathbf{R};\mathbf{r}_\pi)=L(\lambda)M(\mu)\Omega(\phi)\ , \tag{14}$$

$$\lambda=(r_1+r_2)/R,\quad 1\le\lambda<\infty$$
$$\mu=(r_1-r_2)/R,\quad -1\le\mu\le 1 \tag{15}$$
$$\phi=\text{azimuthal angle},\quad 0\le\phi<2\pi\ .$$

The wave equation then separates into the three following second-order differential equations;

TABLE II. Bond lengths and values of n_0 for different centers.

Bond Z_1—Z_2	Molecule	R (in units of a_e)	R (Å)	$n_0(Z_1)$	$n_0(Z_2)$
H—H	H_2	1.401 65	0.742	8	
C—H	CH_4	2.066 50	1.094	31	7
C—H	CH_3OH	2.071 00	1.096	31	7
N—H	NH_3	1.916 38	1.014	33	7
N—H	N_2H_4	1.931 33	1.022	33	7
O—H	H_2O	1.808 84	0.957	34	7
O—H	CH_3OH	1.806 90	0.956	34	7
O—C	CO_2	2.194 40	1.161	30	24

$$\frac{d}{d\lambda}(\lambda^2-1)\frac{dL}{d\lambda}+\left[-A+p^2(\lambda^2-1)-\frac{m^2}{\lambda^2-1}+R(Z_1+Z_2)\lambda\right]L=0\ , \tag{16}$$

$$\frac{d}{d\mu}(1-\mu^2)\frac{dM}{d\mu}+\left[A-p^2(1-\mu^2)-\frac{m^2}{1-\mu^2}-R(Z_1-Z_2)\mu\right]M=0\ , \tag{17}$$

and

$$\left[\frac{d^2}{d\phi^2}+m^2\right]\Omega=0\ , \tag{18}$$

where A is a separation constant and $p=(-W/2)^{1/2}$. The eigenequation for λ is often known as the "outer" equation and that for μ as the "inner" equation. The solutions of these two equations take the form of semianalytical series expansions[12,14]

$$L(\lambda)=(\lambda^2-1)^{m/2}(\lambda+1)^{\sigma}e^{-p\lambda}\sum_{t=0}^{t_m}g_t\left[\frac{\lambda-1}{\lambda+1}\right]^t\ , \tag{19}$$

$$M(\mu)=\sum_{s=0}^{s_m}f_sP_{m+s}^{m}(\mu)\ , \tag{20}$$

with m non-negative, $\sigma=R(1+q)/2p-m-1$, and $q=Z_2/Z_1$ $(Z_2\geq Z_1)$. $P_{m+s}^{m}(\mu)$ are the unnormalized Legendre functions[15] and the coefficients g_t and f_s are to be determined. The eigenfunction for the angular coordinate is simply

$$\Omega(\phi)=\exp(\pm im\phi)\ . \tag{21}$$

In order to calculate the eigenenergy as a function of R, the solutions (19) and (20) must be substituted into Eqs. (16) and (17), respectively, from which three-term recurrence relations for the series coefficients are obtained. For example, if the outer equation is considered,

$$\alpha_j g_{j-1}+\beta_j g_j+\gamma_j g_{j+1}=0\ , \tag{22}$$

with $j=0,1,2,3,\ldots$, and α, β, and γ are functions of j, p, A, R, Z_1, Z_2, and m. The quantum numbers n and l enter implicitly through the values of p and A. If g_{-1} is set to zero and Eq. (22) is divided throughout by g_0, the following equation is obtained;

$$G(p,A)=\beta_0+\gamma_0 g_1/g_0=0\ , \tag{23}$$

where g_1 and g_0 can be expressed in higher j terms using the recurrence relation, and so $G(p,A)$ becomes a continued fraction which is said to be "chained" at a value of j for which the fraction is terminated. This value is determined by the convergence of $G(p,A)$, and it has been shown[16,17] that the series solution for λ allows $G(p,A)$ to converge at a finite value of j for both small and large values of p. A similar approach for the inner equation will result in a second continued fraction,

$$F(p,A)=0\ . \tag{24}$$

Simultaneous solutions of (23) and (24) exist only for discrete values of p and A, from which the eigenenergies can be obtained. These solutions are found by initial guesses for p and A from which more accurate values can be obtained using a quadratically convergent Newton-Raphson scheme. At $R=0$, the first initial guess for p and A can be obtained from the eigenparameters for the united atom, and subsequent guesses are obtained by extrapolation. If the potential curve $E(R)$ is calculated starting from large R, the first two initial estimates for p and A are given by large-R asymptotic expansions, and again further guesses at other values of R can be extrapolated. The large-R asymptotic expansions for p and A are of the order of R^{-6}. More accurate initial guesses require more complex expansions,[18] but this generally only saves a few iterations before arriving at an acceptable solution.

Having calculated p and A as a function of the internuclear separation, it is possible to go back to Eqs. (23) and (24) and obtain the coefficients g_t and f_s and hence to obtain the complete expression for the wave function at any value of R.

G. Eigenenergy calculations

The Schrödinger equation (10) for the two-center system without electrons was solved and the energy curves were calculated using a code developed by Power[19] to investigate one-electron diatomic molecules. The input to the code consists of the two nuclear charges (Z_1 and Z_2), the united atom quantum numbers of the chosen state (n,l,m), the range of internuclear separations for which $W(R)$ is required, and accuracy criteria for the convergence of the successive iterations to p and A and for the convergence of the continued fractions and their derivatives.

The accuracy of the values of p and A obtained by simultaneously solving the two continued fractions was initially set to ten decimal places. For quantum states with a low principal quantum number, n, this accuracy setting allowed a rapid convergence to the correct values of p and A, but for higher quantum states the convergence was much slower, and in some cases a reduced accuracy setting (to a minimum of five decimal places) was required. The large-R asymptotic expansions proved to be very reliable. However, the use of extrapolation to obtain initial guesses necessitated extreme caution especially in a range of R where the energy curve has a minimum or a rapid change of slope. For such cases it was important to use sufficiently small increments of R to follow the curve, or else the initial guess either did not result in convergence or converged to a solution of a different quantum state.

The accuracy and convergence rate of the continued fractions and their derivatives also depends on the choice of quantum state. For increasing quantum numbers, the pairs of eigenparameters get closer and closer together, and consequently if F and G are to be continuous, their derivatives must become smaller which in turn slows down the convergence. The initial accuracy for the continued fractions was set to five decimal places, but again the accuracy was reduced (to a minimum of two decimal places) when necessary.

A problem encountered in the calculation of the pion eigenenergies was the occasional "jumping" from a correct pair of eigenparameters for the state of interest to a totally different pair belonging to a different eigenstate. This phenomenon, known as the quasicrossing of energy curves,[19–21] is manifested by a sudden discontinuity in $W(R)$ at a particular value of the internuclear separation. A quasicrossing is the result of the interaction between two states of the same symmetry and of almost equal energy, which belong to each of the two potential wells below the barrier. Such interactions occur by virtue of symmetry and for homonuclear systems may be ignored since the two states involved are identical. However, for heteronuclear systems, quasicrossings occur by "accident" and it is important to be aware of their presence; otherwise, incorrect eigenparameters may unknowingly be obtained. Discontinuities in the energy curves can be detected directly by visual inspection of $W(R)$ or else by comparing the calculated eigenenergies at zero and infinite separations with the known energies of the united atom and separated atom systems. The problem of quasicrossings was found to be most severe for the higher quantum states where the energy separations between states becomes extremely small, hence encouraging the process.

H. Classification of bonding and antibonding orbitals

The shape of the potential curve $E(R)$ for a pion quantum state can be used to classify bonding molecular orbitals[22] and to find in which range of R they are likely to occur. At R close to zero, the curve of $E(R)$ will go to infinity on account of the nuclear repulsion term, and at infinite R, it will tend to a separated atom energy. If $E(R)$ decreases monotonically between the two limits, the orbital will be repulsive at all values of R and will decrease in energy as the internuclear separation increases. If, however, the curve has a minimum value at a distance $R_{\min}$, the pion orbital will be stable over a range of R on either side of $R_{\min}$, and the nuclei will be attracted to each other by the pion charge density between the two centers. The deeper the curve is for a bonding state, the more stable the state will be. The lower quantum states tend to be the most stable, as the higher states are of lower energy, with much shallower minima.

The two-center systems of H—H, C—H, N—H, O—H, and O—C were investigated for internuclear separations ranging from zero to $700a_\pi$. This range covers typical bond lengths associated with any pair of centers used. Quantum states up to the united atom equivalent of n_0 were examined.

The number of bonding states for the H—H systems is tabulated in Table III. The values in this table correspond to the number of m states which are bonding for all allowed combinations of n and l. It can be seen that the number of bonding states is considerably less than the number of allowed states. The C—C system was also shown to having bonding states.

The analysis of all the heteronuclear systems showed that all the states were antibonding, as the energy curve always decreased monotonically from the united atom limit at $R=0$ to $R=700a_\pi$, where $E(R)$ approached the separated atom energy.

I. Verification of the Born-Oppenheimer approximation

An accurate analysis of the Born-Oppenheimer approximation requires the evaluation of the extra term introduced into the Schrödinger equation by the separation of the nuclear and pion wave functions. This is possible for simple molecular wave functions, using a linear combination of atomic orbitals,[23,24] but using the series expansion solutions, not only is the energy dependent on R, but so are the coefficients g_t and f_s (which may be numerous for certain states). The calculation of the partial derivatives of these coefficients would be very difficult and very inaccurate.

The Born-Oppenheimer approximation is valid for electrons because they move so much faster than the nuclei vibrate about their position of equilibrium, that the nuclei can be considered as "frozen." The same would be true for pions if it can be shown that the average kinetic energy of the pion in a given state is substantially greater than

TABLE III. Bonding states for H—H.

	n												
l	13	12	11	10	9	8	7	6	5	4	3	2	1
12	11												
11	9	9											
10	6	8	9										
9	3	5	7	8									
8	0	2	4	6	7								
7	0	0	1	3	5	6							
6	0	0	0	1	2	4	5						
5	0	0	0	0	0	1	3	4					
4	0	0	0	0	0	0	1	2	4				
3	0	0	0	0	0	0	0	0	1	3			
2	0	0	0	0	0	0	0	0	0	1	2		
1	0	0	0	0	0	0	0	0	0	0	0	1	
0	0	0	0	0	0	0	0	0	0	0	0	0	0

the molecular vibrational energy associated with that state.

Using the virial theorem,[25] it is possible to show that the average kinetic energy of the pion can be derived from the potential curve $E(R)$, by the relation[8]

$$E^{\mathrm{av}}_{\mathrm{kin}} = -E - R(dE/dR) , \tag{25}$$

where dE/dR is taken at the center separation.

The vibrational energy may be estimated for bonding states by expanding $E(R)$ in a power series about the equilibrium position at R_{min}. Thus,

$$E = -D + k(R - R_{\mathrm{min}})^2/2 + \cdots , \tag{26}$$

where D is the dissociation energy and k is a constant. If higher-order terms are ignored, then to a first approximation, the force $(-dE/dR)$ is proportional to the displacement (R), and for vibrations of small amplitude, the equation becomes that of simple harmonic motion. The frequency of the motion is

$$\nu = (k/M)^{1/2}/2\pi \tag{27}$$

and the vibrational energy is therefore

$$E_{\mathrm{vib}} = \hbar(k/M)^{1/2} . \tag{28}$$

For a more accurate estimation of E_{vib}, a Morse potential[8] can be used to describe $E(R)$ close to the equilibrium, instead of the quadratic used above.

The average pion kinetic energy for a selection of states of the H—H system was evaluated using Eq. (25) at an internuclear separation of $500a_\pi$. The states chosen were bonding states, and values of N close to n_0 were examined more closely. dE/dR was found by using a nine-point differentiation formula derived from a similar three-point formula by Dorn and McCracken.[26] Since $E(R)$ was fairly linear in the region of $R = 500a_\pi$, the accuracy of the technique was acceptable. The energies were obtained in mesoatomic units and later converted into units of eV. Values of $E^{\mathrm{av}}_{\mathrm{kin}}$ are presented in Table IV together with the united atom and separated atom quantum numbers of the states, the binding energies, and the values of R_{min}.

The vibrational energy of the chosen states was found by a minimization of the sum of the squares of the differences between the true values of E and the values of E obtained from (28), in order to find a suitable value for k. Calculated values of k and E_{vib} are also presented in Table IV together with the ratio between E_{vib} and $E^{\mathrm{av}}_{\mathrm{kin}}$ expressed as a percentage. Thus the Born-Oppenheimer approximation is valid for pions to an accuracy of $\sim 5\%$, except for the lowest state.

An estimation of $E_{\mathrm{vib}}/E^{\mathrm{av}}_{\mathrm{kin}}$ was obtained for the ground state of the hydrogen molecular ion (for which the Born-Oppenheimer approximation is known to be valid) in order to test the above numerical techniques. The average kinetic energy of the electron was found to be 16.37 eV and the vibrational energy to be 0.287 eV (2% of

TABLE IV. $E^{\mathrm{av}}_{\mathrm{kin}}$ and E_{vib} for various states of the H—H system.

n	l	m	N	K	R_{min} (in units of a_π)	E_{binding} (eV)	$E^{\mathrm{av}}_{\mathrm{kin}}$ (eV)	k (eV/m^{-2})	E_{vib} (eV)	$E_{\mathrm{vib}}/E^{\mathrm{av}}_{\mathrm{kin}}$ (%)
1	0	0	1	0	2	−3478.2	3464.3	1.6×10^{28}	1167.9	34
3	2	2	3	0	18	−398.7	384.9	1.7×10^{25}	37.8	10
4	3	3	4	0	32	−230.4	216.5	2.6×10^{24}	14.7	7
5	4	4	5	0	53	−152.4	138.6	2.4×10^{23}	4.5	3
6	5	3	5	1	49	−152.6	138.4	2.1×10^{24}	13.3	10
7	6	4	6	1	69	−110.3	96.0	7.5×10^{23}	7.9	8
8	7	4	6	1	103	−110.3	96.0	1.1×10^{23}	3.0	3
9	8	5	7	1	134	−84.8	70.5	4.3×10^{22}	1.9	3
10	7	0	6	3	109	−110.3	96.0	1.2×10^{23}	3.2	3
10	7	3	8	2	125	−67.9	54.2	1.0×10^{23}	2.9	5
10	9	0	5	4	104	−153.3	137.6	6.3×10^{23}	7.2	5
10	9	7	9	1	151	−56.9	42.6	6.1×10^{22}	2.2	5
11	8	0	7	4	113	−85.1	70.1	3.5×10^{23}	5.4	8
11	8	4	9	2	157	−56.5	43.0	5.1×10^{22}	2.0	5
11	10	0	6	5	120	−111.5	94.7	7.3×10^{23}	7.8	8
11	10	8	10	1	185	−48.7	34.6	3.0×10^{22}	1.6	6
12	9	0	7	4	146	−85.1	70.1	9.2×10^{22}	2.8	4
12	9	5	10	2	193	−48.4	34.9	2.7×10^{22}	1.5	4
12	11	0	6	5	148	−111.5	94.7	2.6×10^{23}	4.6	5
12	11	9	11	1	223	−42.7	28.6	1.7×10^{22}	1.2	4
13	9	0	8	4	180	−68.2	53.9	2.6×10^{22}	1.5	3
13	9	3	10	3	198	−48.4	34.9	3.2×10^{22}	1.6	5
13	12	0	7	6	168	−86.6	68.3	2.8×10^{23}	4.8	7
13	12	10	12	1	264	−38.0	24.1	9.8×10^{21}	0.9	4
15	14	0	8	7	225	−70.9	50.4	1.2×10^{23}	3.1	6
17	16	0	9	8	290	−60.7	36.8	5.3×10^{22}	2.1	6
19	18	0	19	9	364	−54.5	20.5	2.7×10^{22}	1.5	7

$E_{\rm kin}^{\rm av}$). The value of the nuclear vibrational energy agrees well with the value of 0.285 eV calculated by Bransden and Joachain.[27]

J. Evaluation of pion two-center wave functions

Having obtained the energy of a pion state from the code described above, it was possible to evaluate the coefficients g_t and f_s and hence define the pion two-center wave function at any internuclear separation. This was done using a code developed by Salin[14] which requires information about the charges of the two centers, the united atom quantum numbers, the internuclear separation (in mesoatomic units), the eigenenergy, and the separation constant. The code represents the three-term recurrence relationship for the outer equation (22), and the equivalent equation for the inner equation, in the form of t_m and s_m linear equations, where t_m and s_m depend on the required accuracy of the wave function. These equations are then transformed into matrix form and solved using a Fortran translation of an ALGOL program written by Martin and Wilkinson.[28] The matrix of the outer equation is tridiagonal and that of the inner equation is tridiagonal for a system of identical nuclei and pentadiagonal for nonidentical nuclei. In the case of identical nuclei, the solution to the inner equation is summed only over odd terms if $l+m$ is odd and only over even terms if $l+m$ is even.

Once the coefficients of the expansions have been obtained, the wave function can be normalized to unity by integration over the confocal elliptic coordinates. The integration over the angular coordinate is trivial and that over the μ coordinate can easily be done analytically by using the orthogonal properties of the associated Legendre polynomials. The integration of the remaining coordinate is more difficult and must be performed numerically.

The wave functions of the lowest bonding and antibonding orbitals of the hydrogen molecular ion were calculated in order to test the code, and showed the expected behavior. The behavior of $E(R)$ against R and contour plots of the wave functions for selected pion states are shown in Fig. 2.

III. THE TWO-CENTER SYSTEM INCLUDING ELECTRONS

A. The Schrödinger equation

The addition of electrons to a simple two-center system will result in an extra potential between the pion and electrons which must be included in the Hamiltonian of the original Schrödinger equation. We assume that the presence of the pion leaves the molecular electron distribution essentially unperturbed and use known electron distributions in order to investigate the effect of the electrons on the pion. To a considerable extent, this assumption is dictated by practical considerations, namely the availability of unperturbed molecular wave functions and the huge complexity of a true self-consistent calculation, but it may also be argued that the pion is moving rapidly through the available states while the electron distribution is relatively undisturbed. This is a good argument if there is instantaneous refilling of electron holes caused by Auger transitions. We have endeavored to investigate the effect of finite refilling times.

Self-consistent[29] and approximate[30] calculations have been carried out for muonic atoms. The partial penetration of electrons through the muon orbit is not significant for light atoms but in heavier atoms is most pronounced for muon orbits with large n or the more eccentric orbits. It is concluded[30] that the largest uncertainty in the calculation of screening corrections in muonic atoms is connected with the incomplete filling of the electron shells.

The Schrödinger equation now becomes

$$\left[-\frac{\nabla_\pi^2}{2}+V(\mathbf{R},\mathbf{r}_\pi)+E_e(\mathbf{r}_\pi)\right]u'(\mathbf{R};\mathbf{r}_\pi)=E'(R)u'(\mathbf{R};\mathbf{r}_\pi)\,, \tag{29}$$

where $E_e(\mathbf{r}_\pi)$ is the pion-electron potential. The wave equation for the nuclear motion (11) will also change because of the addition of a modified potential-energy curve $E'(R)$ and a new potential $E_e(R)$ between the electrons and the nuclei,

$$\left[-\frac{\nabla_R^2}{2M}+E'(R)+E_e(R)\right]v'(\mathbf{R})=\epsilon' v'(\mathbf{R})\,. \tag{30}$$

B. Electron wave functions

In order to calculate pion-electron potentials, it is necessary to obtain electron wave functions in a molecular configuration around the bonds of interest. For the H-H bond, this is possible by using the total electron wave function for the diatomic molecule H_2. However, for the remaining bonds (C—H, N—H, O—H, and O—C), true diatomic molecules do not exist and so it is necessary to extract the electron wave function from wave functions for large molecules (i.e., CH_4, NH_3, H_2O, CO_2, CH_3OH, and N_2H_4).

A convenient description of electron wave functions is available by using summed "contractions" over a Gaussian basis set.[31,32] Tables of coefficients (C) and exponents (α) exist for an extensive collection of molecules,[29] together with data on the positions of the nuclei in the molecule, the bond lengths, and the bond orientations.

The wave function of the ith contraction for a center k may be written as

$$\rho_{ik}=\sum_j {}_kN_{ij}\,{}_kC_{ij}f(X_k,Y_k,Z_k)\exp(-{}_k\alpha_{ij}R_k^2)\,, \tag{31}$$

where the function $f(X_k,Y_k,Z_k)$ is defined as

$$f(X_k,Y_k,Z_k)=\begin{cases}1 & \text{for } S \text{ contractions}\\ X_k & \text{for } PX \text{ contractions}\\ Y_k & \text{for } PY \text{ contractions}\,,\\ Z_k & \text{for } PZ \text{ contractions}\end{cases} \tag{32}$$

$X_k=x-x_k$, etc., (x_k,y_k,z_k) are the Cartesian coordinates of the kth center, and $R_k=(X_k^2+Y_k^2+Z_k^2)^{1/2}$. The normalization constant ${}_kN_{ij}$ is such that

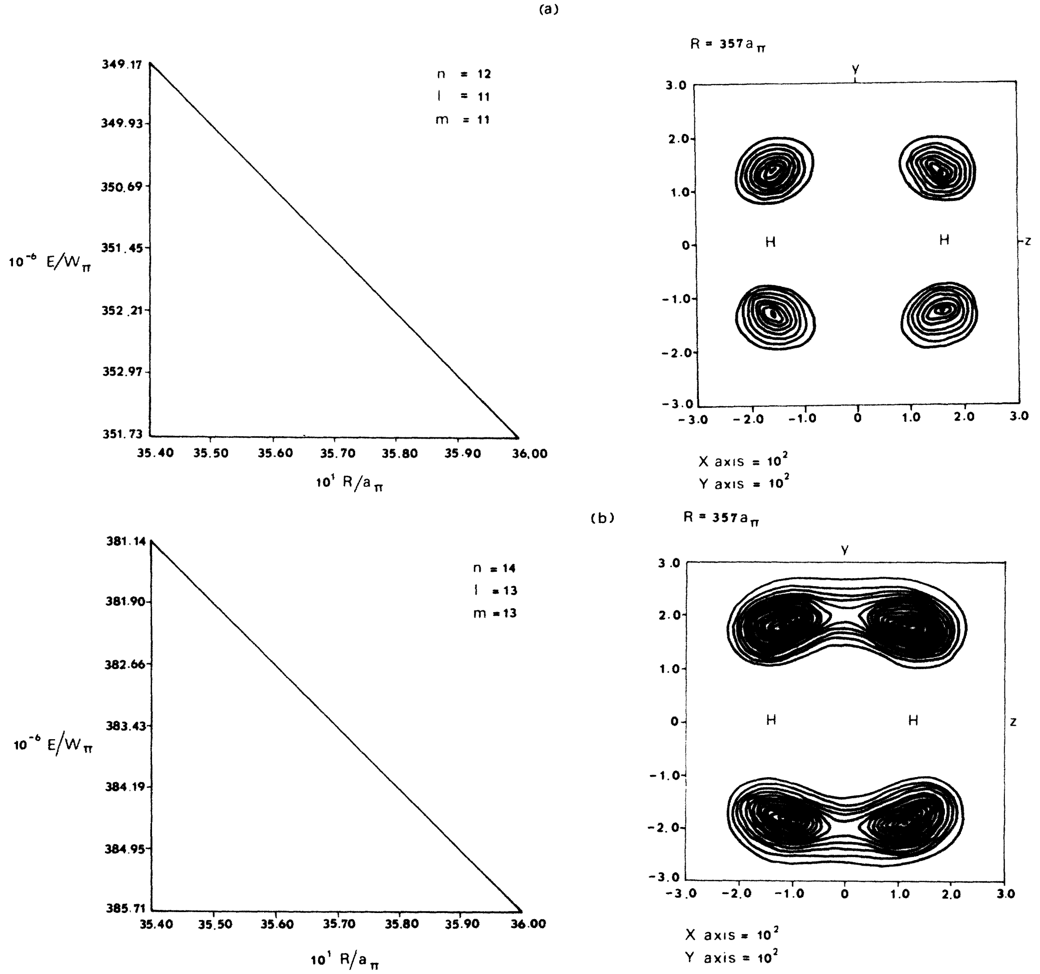

FIG. 2. Plots of $E(R)$, in units of W_π, and of pion wave functions: (a) H—H, (b) H—H, (c) C—H, (d) O—H.

$$\int d\tau_e \rho_{ik}^2 = 1 \tag{33}$$

and can be evaluated for S and P contractions by the formulas (dropping all subscripts)

$$N^2 = (2\alpha/\pi)^{3/2} \tag{34}$$

for S contractions and

$$N^2 = (2^{7/2}\alpha^{5/2})/\pi^{3/2} \tag{35}$$

for P contractions.

The 1s electron wave function is found by summing the $S1$ and $S2$ contractions, the 2s wave function by summing the $S3$ and $S4$ contractions, and the $1p_x$, $1p_y$, and $1p_z$ wave functions by summing the $PX1$ and $PX2$ contractions, the $PY1$ and $PY2$ contractions, and the $PZ1$ and $PZ2$ contractions, respectively.

The total electron density for a two-center system ($k=2$) is

$$\sum_{k=1}^{2} \sum_{i} a_{ik} \rho_{ik}^2 , \tag{36}$$

where a_{ik} is the Mulliken charge[33] associated with the wave function of the ith contraction of the kth center.

Contour plots of the electron densities for H_2, CH_4, H_2O, and CO_2 are presented in Fig. 3 together with sections along the z axis. Similar calculations have been made for C—H and O—H bonds extracted from CH_3OH. H_2 and CO_2 are linear molecules, whereas the remainder are nonlinear and have bond orientations which are not along the z axis, used to define the electron configuration. The bonds in the latter case can be reoriented along the desired axis by transforming the Cartesian coordinates used in the description of the electron wave functions, with a rotation matrix

$$\begin{bmatrix} \cos\theta\cos\phi & -\sin\theta & \cos\theta\sin\phi \\ \sin\theta\cos\phi & \cos\theta & \sin\theta\sin\phi \\ -\sin\phi & 0 & \cos\phi \end{bmatrix} ,$$

where ϕ is the angle made between the bond and z axis, and θ is the angle made between the projection of the bond in the x-y plane and the x axis.

C. The pion-electron potential

Using the summed contractions of Gaussian basis sets to obtain the electron wave functions, as described above,

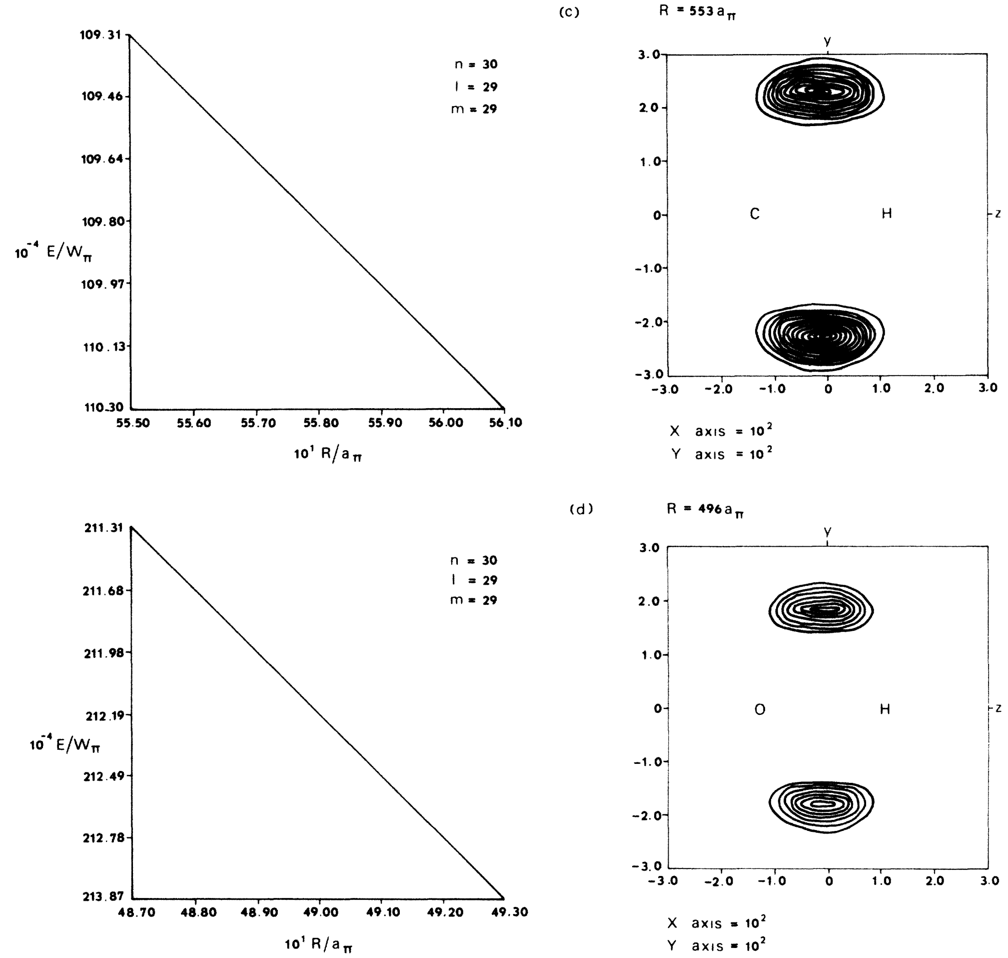

FIG. 2. (*Continued*).

the pion-electron potential can be calculated as a function of the pion position by evaluating the following three-dimensional integral:

$$E_e(\mathbf{r}_\pi)=\sum_{k=1}^{2}\sum_{i}\int d\tau_e \rho_{ik}^{*}\frac{a_{ik}}{|\mathbf{r}_\pi-\mathbf{r}_e|}\rho_{ik}\,, \tag{37}$$

where $\mathbf{r}_\pi$ and $\mathbf{r}_e$ are the pion and electron position vectors. This potential will be repulsive and will therefore be of opposite sign to the attractive potential $C(\mathbf{r}_\pi)$ between the pion and the nuclei.

Although the electron wave functions were originally described in Cartesian coordinates, the integration was performed by first transforming to confocal elliptic coordinates, using the transformation equations

$$\begin{aligned} x&=\frac{R}{2}(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\sin\phi\,,\\ y&=\frac{R}{2}(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\cos\phi\,,\\ z&=\frac{R}{2}\lambda\mu\,, \end{aligned} \tag{38}$$

with the two nuclei at $(0,0,\pm\frac{1}{2}R)$, and then integrating using a Gauss-Laguerre quadrature for λ and Gauss-Legendre quadrature for μ and ϕ. Integrations using both pion and electron wave functions, such as overlap integrals, could then be done using the same quadrature techniques.

The accuracy of the integration was dependent upon the number of pivotal points used for each of the coordinates Unfortunately, increased accuracy requires a greater number of points, which poses problems with the time taken by the calculations, and hence a compromise between accuracy and time had to be found. The number of times the integrand must be calculated for one integration is equal to the product of the number of pivotal points used for the three coordinates. The functional form of the integrand is complicated, as it contains the sum over 20 contractions (in the worst case of O—C) and the transformation of the coordinates system. Furthermore, for centers which are not orientated along the z axis, the use of the rotation matrix was also necessary. Time proved to be a limiting factor, especially since E_e was required in a plane at the very least (and preferably in all space). The best choice of the number of pivotal points was 32 for the integrations of the λ and μ coordinates and eight points for the less important angular coordinate. The accuracy of the integration technique was tested by computing the

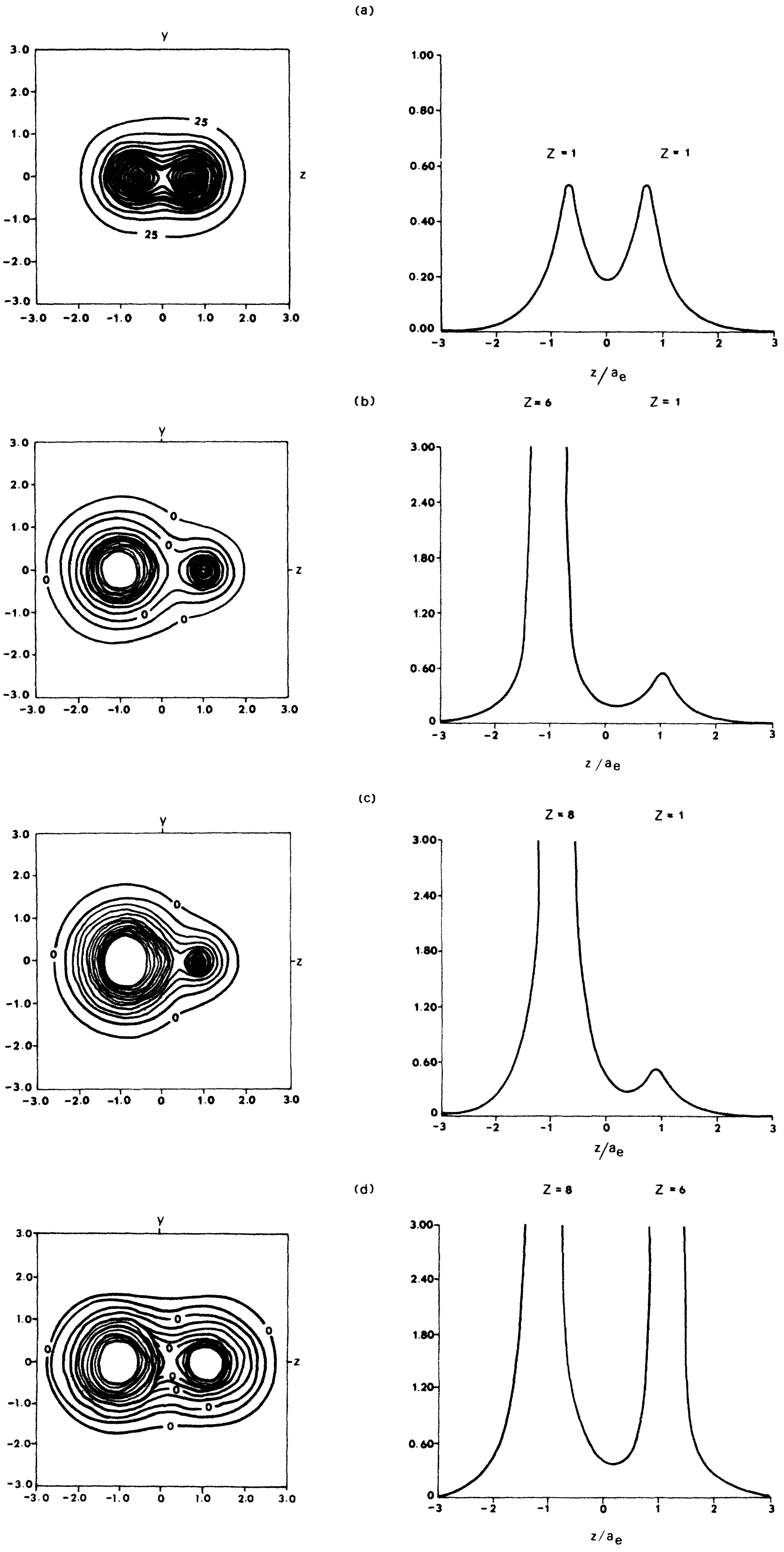

FIG. 3. Plots of the electron densities derived from group-*A* molecules: (a) H—H, (b) C—H, (c) O—H, (d) O—C.

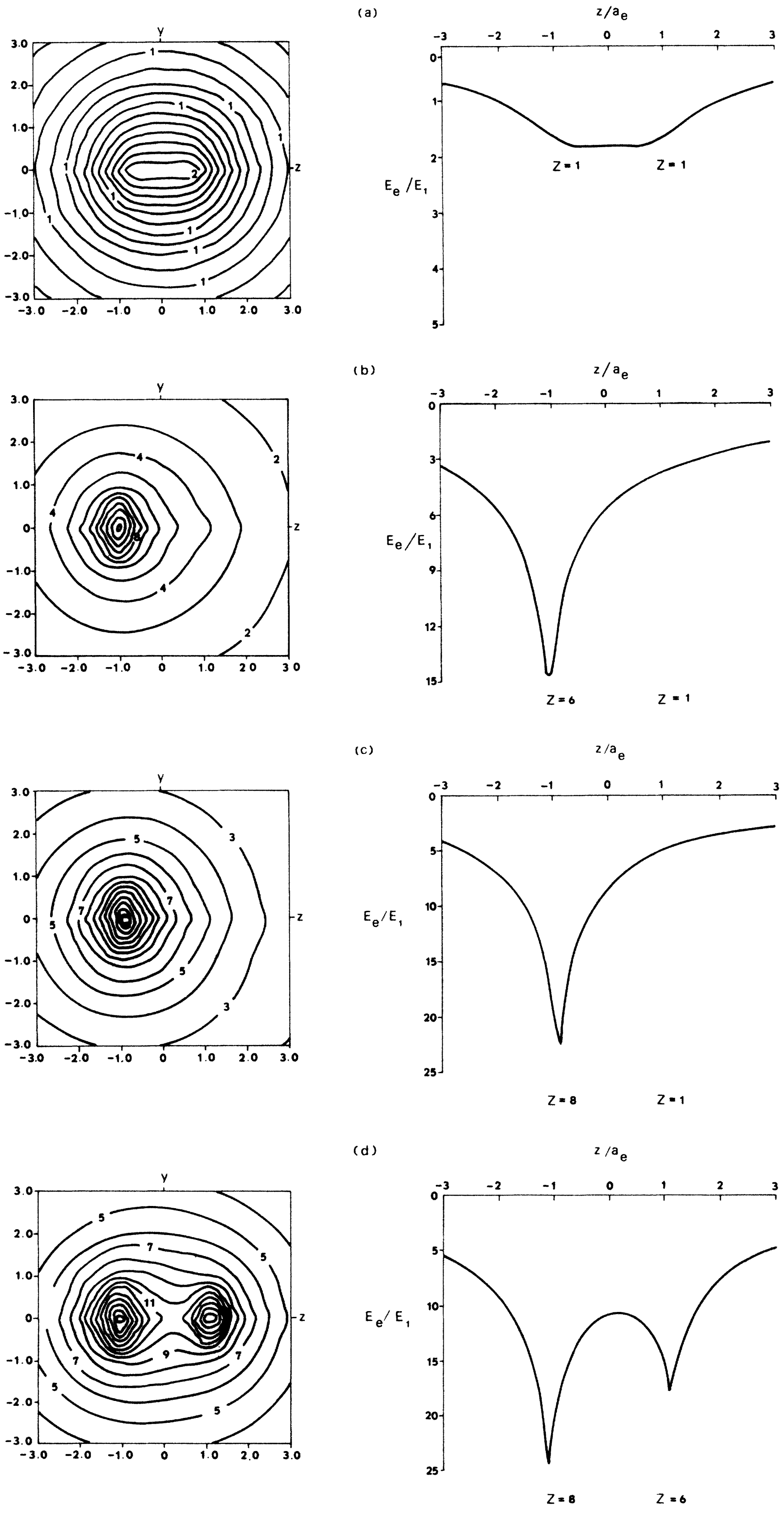

FIG. 4. Plots of $E_e(\mathbf{r}_\pi)$, in units of E_1, for group-A molecules: (a) H—H, (b) C—H, (c) O—H, (d) O—C.

TABLE V. Comparison of exact charge with calculated charge.

Bond	Molecule	Exact charge	Integrated charge
H—H	H_2	2.000	2.000
C—H	CH_4	7.553	7.544
N—H	NH_3	8.577	8.566
O—H	H_2O	9.386	9.374
O—C	CO_2	13.707	13.696

charge normalization integrals (36) for the different centers. The results are tabulated in Table V and illustrate the adequacy of the choice of pivotal points.

Contour plots of E_e in the y-z plane and sections along the bond axis are presented for group-A molecules in Fig. 4. The scales used for the graphs are identical to the ones used in Fig. 1, for comparison with the pion-nuclear potential. The signs of the two potentials are, however, opposite. The sum of the pion-nuclear and pion-electron potentials is shown in Fig. 5. The same calculations have been made for group-B molecules. There are differences which can be seen in the contour plots but not in the sections on the scale of these figures.

The calculations of E_e were checked by considering the behavior of the potential close to and away from the centers. As the pion moves away from the centers, the magnitude of the pion-electron potential will become equal to that of the pion-nuclear potential, since at this distance the two potentials look identical, although opposite in sign. Hence, for large distances, the $1/r_\pi$ behavior of V and E_e cancel each other out, as shown in Fig. 5. Close to the centers, E_e must approximate the potential between a pion and an equivalent atom. Similar calculations have been made using electron wave functions for atoms obtained from self-consistent-field (SCF) theory.[34] The values of E_e at the position of the centers were compared using the two different approaches. Potentials calculated from atomic electron configurations defined using the same Gaussian basis set used previously were also calculated for comparison. The results, found in Table VI, show that the potentials are comparable and that they are larger for the molecular configurations, as would be expected because of the greater number of electrons and concentration of charge. The atomic Gaussian basis-set calculations are closer to the atomic SCF calculations. The behavior of E_e between the two limits is both smooth and regular.

The pion-electron potential was also calculated for group-A molecules after removing the $1s$ electrons ($S1$ and $S2$ contractions) and the valence electrons ($PX1$, $PX2$, $PY1$, $PY2$, $PZ1$, and $PZ2$ contractions) in order to see the contribution to E_e by the different electrons. Results are shown in Fig. 6. Since hydrogen only contains a $1s$ electron, it was not removed in these calculations (hence the omission of H_2 in Fig. 6). It can be seen that the $1s$ electrons make an important contribution to the pion-electron potential close to the nuclear centers. Omission of the $1p$ electrons has a much smaller effect close to the centers and a large effect away from the centers.

The increase in the barrier height as a consequence of the addition of the electrons is presented numerically in Table VII which gives the barrier heights of the original pion-nuclear potential and of the new potential including the electrons. Also tabulated are the barrier heights after removal of the $1s$ electrons from carbon, nitrogen, and oxygen centers. This is of interest because, physically, electron states are depleted in the pion cascade process due to Auger transitions and the states are subsequently replenished by electrons from higher orbitals.[35] The rate of electron refilling is thought to be extremely rapid, except for core electrons in light nuclei.[36,37] We expect that, on average, one K-shell electron is missing from C,N,O in the light molecules we are considering. Thus, the true situation should be between the two cases we have examined, i.e., all electrons present or both K-shell electrons absent.

D. Parametrization of $V+E_e$

An attempt was made to parametrize the sum of the pion-nuclear and pion-electron potentials to facilitate calculations with this total potential. The following functions were tried:

$$V+E_e=-(Z_1/r_1)\exp(-Ar_1)-(Z_2/r_2)\exp(-Br_2) \tag{39}$$

$$=-[(Z_1-C)/r_1]\exp(-Ar_1)-[(Z_2-D)/r_2]\exp(-Br_2) \tag{40}$$

$$=-(Z_1/r_1)\exp(-Ar_1^2)-(Z_2/r_2)\exp(-Br_2^2) \tag{41}$$

$$=-(Z_1/r_1)+C\exp(-Ar_1)-(Z_2/r_2)+D\exp(-Br_2)\,. \tag{42}$$

TABLE VI. Comparison of E_e calculated from different electron configurations.

Center	SCF (atom) (eV)	Gaussian basis set (atom) (eV)	Gaussian basis set (molecule) (eV)
H		33	49 (H_2)
C	316	385	398 (CH_4) 484 (CO_2)
N	403	481	526 (NH_3)
O	521	584	608 (H_2O) 663 (CO_2)

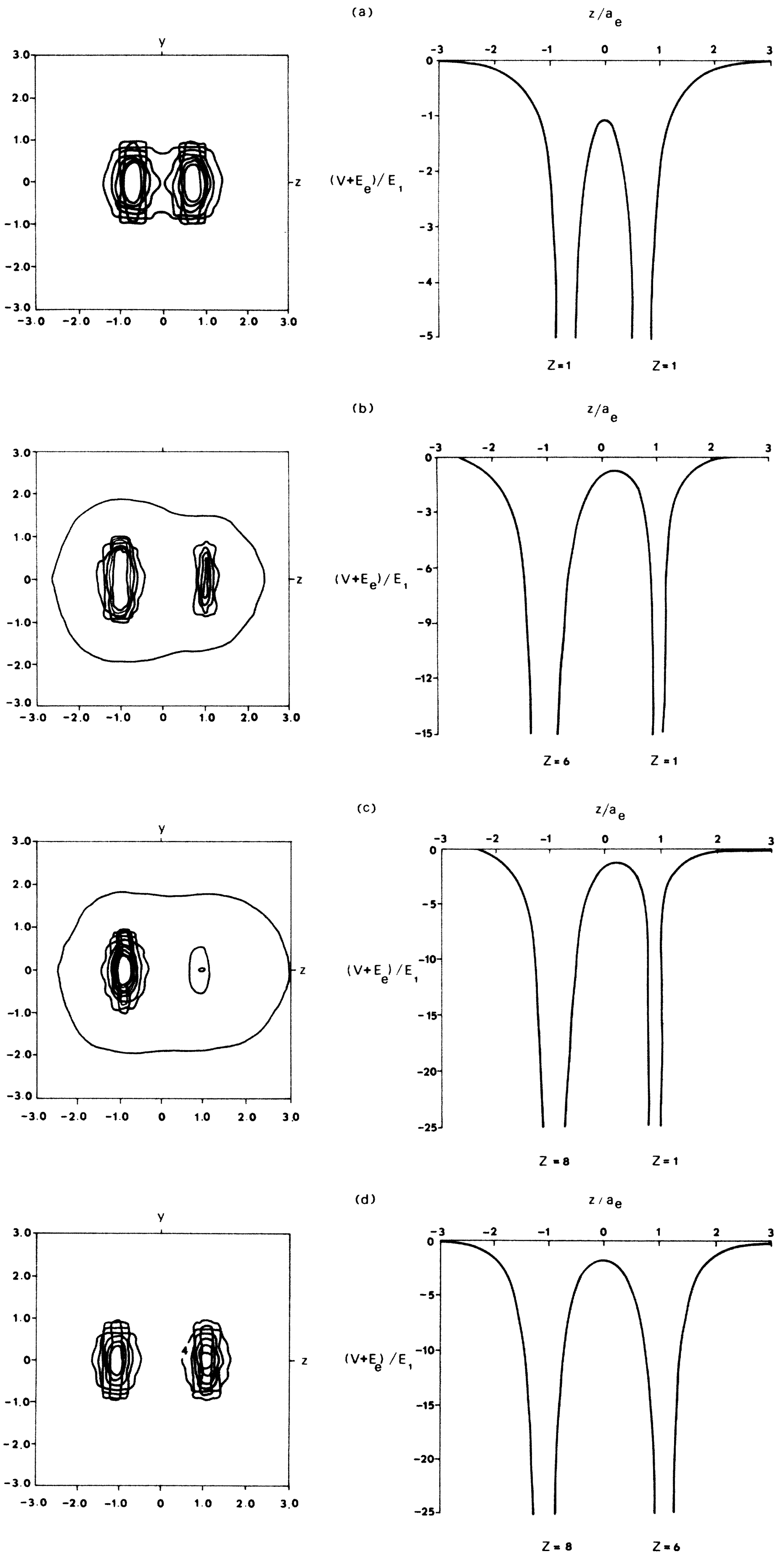

FIG. 5. Plots of $V(\mathbf{r}_\pi)+E_e(\mathbf{r}_\pi)$, in units of E_1, for group-A molecules: (a) H—H, (b) C—H, (c) O—H, (d) O—C.

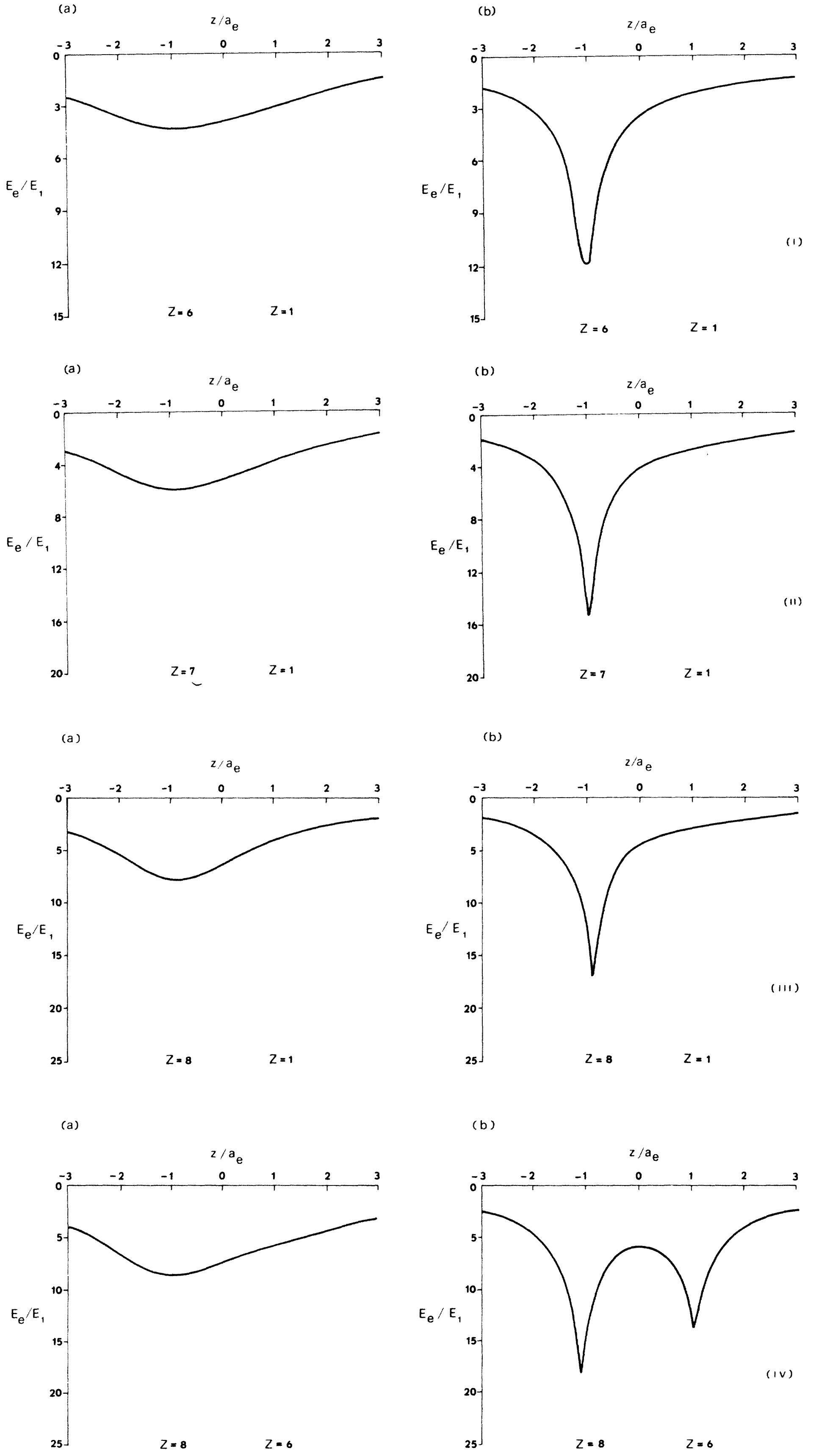

FIG. 6. Plots of $E_e(\mathbf{r}_\pi)$, in units of E_1, for group-A molecules, (a) without 1s electrons and (b) without 1p electrons: (i) C—H, (ii) N—H, (iii) O—H, (iv) O—C.

TABLE VII. Barrier heights for different potentials.

Bond	Molecule	Height of V/E_1	Height of $(V+E_e)/E_1$	Height of $(V+E_e)/E_1$ (without 1*s* electrons)
H—H	H_2	−2.854	−1.075	
C—H	CH_4	−5.765	−0.743	−2.204
	CH_3OH	−5.753	−0.937	
N—H	NH_3	−6.945	−0.950	−2.523
	N_2H_4	−6.894	−1.060	
O—H	H_2O	−8.115	−1.212	−2.868
	CH_3OH	−8.124	−1.272	
O—C	CO_2	−12.699	−1.868	−5.511

The constants were found by a least-squares minimization routine.

The Gaussian potential (41) and the potential (42) were the least satisfactory of the chosen functions, especially in the region between the two centers. We refer to the potential (40) as a "screened" Yukawa potential because the strength of the charges on the two centers has been reduced. Both the Yukawa and the screened Yukawa potentials were very adequate, the latter being slightly superior because of the extra parameters. The exponential terms in both of these potentials describe the fall to zero of $V+E_e$ away fom the centers very well, while, closer to the centers, the Coulomb terms dominate. Values of the fitted constants are listed in Tables VIII and IX for the Yukawa potential and the screened Yukawa potential. The parameters were found using units of a_e and E_1 for length and energy, and also in mesoatomic units for the Yukawa potential. The differences between the parameters for group-*A* and group-*B* molecules are significant.

E. Density of atomic states

The increase in the height of the potential barrier caused by the addition of the electrons will necessarily result in an increase in the number of atomic states centered on either of the two nuclei. Hence the value of n_0 which corresponds to the transition from atomic to molecular states requires a new analysis.

The derivation of the original formula for n_0 assumes that the energies of the atomic states are given by the simple Bohr formula, valid for a Coulomb potential. The new potential in the vicinity of one center is no longer a Coulomb potential, but a Yukawa potential. However, the large separation between the two centers implies that the binding energies may still be estimated by the Bohr equation, with a slight modification for screening.

If $(V+E_e)_{\max}$ is the height of the potential barrier including the effect of the electrons, then the value of $n_0(Z_1)$ for the heavier of the two nuclei (Z_1) can be found from

$$(V+E_e)_{\max} = -\tfrac{1}{2}(Z_1/N_1)^2 - \sigma_2/R\ , \tag{43}$$

where σ_2 is the part of the nuclear charge of the lighter of the two nuclei (Z_2) which is not screened by the electrons,

$$\sigma_2 = Z_2 - \delta_2\ ,$$

δ_2 is the sum of the Mulliken charges on nucleus Z_2, and R is the internuclear separation. The value of $n_0(Z_2)$ is given by a similar expression for the lighter nucleus,

TABLE VIII. Parameters of Yukawa potential.

Bond	Molecule	*A* (in units of a_e^{-1})	*B* (in units of a_e^{-1})	$A\times10^{-2}$ (using mesoatomic units)	$B\times10^{-2}$ (using mesoatomic units)
H—H	H_2	1.359	1.359	0.535	0.535
C—H	CH_4	2.087	1.463	0.772	0.541
	CH_4[a]	0.755	0.860	0.279	0.318
	CH_3OH	1.977	1.182	0.732	0.437
N—H	NH_3	2.201	1.408	0.813	0.519
	NH_3[a]	0.933	0.685	0.345	0.253
	N_2H_4	2.146	1.210	0.793	0.446
O—H	H_2O	2.327	1.212	0.861	0.451
	H_2O[a]	1.104	0.385	0.408	0.142
	CH_3OH	2.307	1.131	0.852	0.417
O—C	CO_2	2.132	1.881	0.785	0.692
	CO_2[a]	0.966	0.467	0.356	0.172

[a] Without 1*s* electrons.

TABLE IX. Parameters for screened Yukawa potential.

Bond	Molecule	A	B	C	D
		(in units of a_e^{-1})		(in units of E_1)	
H—H	H_2	1.452	1.452	−0.038	−0.038
C—H	CH_4	1.743	1.687	0.790	−0.025
	CH_4[a]	0.813	0.689	−0.171	0.020
	CH_3OH	1.540	1.380	0.998	−0.011
N—H	NH_3	1.902	1.609	0.705	−0.018
	NH_3[a]	1.005	0.472	−0.210	0.027
	N_2H_4	1.787	1.402	0.839	−0.012
O—H	H_2O	2.011	1.426	0.701	−0.017
	H_2O[a]	1.306	−0.077	−0.482	−0.078
	CH_3OH	1.976	1.328	0.734	−0.011
O—C	CO_2	1.837	1.426	0.855	0.849
	CO_2[a]	0.937	0.410	0.198	0.215

[a] Without 1s electrons.

$$(V+E_e)_{\max}=-\tfrac{1}{2}(Z_2/N_2)^2-\sigma_1/R \ . \tag{44}$$

Usually there is no charge from the second nucleus ($\sigma_1=0$) since it is totally screened by the electrons. However, if the 1s electrons are removed, some of the nuclear charge becomes exposed and must be considered. From the values of the barrier heights in Table VII, values of n_0 were recalculated for the bonds extracted from the different molecules. Results are tabulated in Table X. Comparison between Table X and Table II shows that, even for hydrogen, the value of n_0 has increased significantly. For the heavier atoms, the increase in n_0 is dramatic, even when depletion of the 1s electron shell is considered.

The energies of the atomic states have been calculated for $K=0$, $m=0$, and the density of states for the bonds taken from group-A molecules are displayed in Fig. 7. The density of states for the original system without electrons is shown for comparison. Many more atomic states are available when the presence of the electrons is taken into account and there is a near-continuum for $Z\geq 6$ near the top of the barrier. The low-lying states in carbon in the C—H system coincide, in the two calculations, up to $N\sim 17$, while discrepancies arise for hydrogen at $N\sim 4$.

The use of a $1/r$ potential must overemphasize the density of states near the top of the barrier. It is possible to calculate the energies of the low-lying states in a single Yukawa potential whose parameter is given in Table VIII. This Yukawa potential represents a parametrization of $V(\mathbf{r}_\pi)+E_e(\mathbf{r}_\pi)$ so it takes account of the presence of the electrons. Results for the $1/r$ potential, without and with electrons, and the Yukawa potential are given in Table XI, for the symmetric H_2 molecule. Although the density of states is reduced in the Yukawa potential, the binding energies are also greatly reduced which will enhance the probability of direct capture and of barrier penetration. In similar calculations with the single Yukawa potentials for $Z=6,7,8$, the number of states below the barrier is always increased compared with the situation when the presence of electrons is ignored, although the effect is not as dramatic as in Fig. 7, and the binding energies of states near to the barrier are greatly reduced.

F. Perturbation calculations

The Schrödinger wave equation (29) can no longer be solved by the same series expansions used to solve the

TABLE X. Recalculation of n_0.

Bond Z_1—Z_2	Molecule	σ_1	σ_2	$n_0(Z_1)$	$n_0(Z_2)$
H—H	H_2	0	0	11	11
C—H	CH_4	0	0.1843	87	14
	CH_4[a]	1.2617	0.1843	48	10
	CH_3OH	0	0.1911	76	13
N—H	NH_3	0	0.2887	92	12
	NH_3[a]	1.1333	0.2887	53	9
	N_2H_4	0	0.3079	86	12
O—H	H_2O	0	0.3859	94	11
	H_2O[a]	1.2276	0.3859	58	8
	CH_3OH	0	0.3827	90	11
O—C	CO_2	0	0.5867	74	52
	CO_2[a]	1.7060	2.5861	45	33

[a] Without 1s electrons.

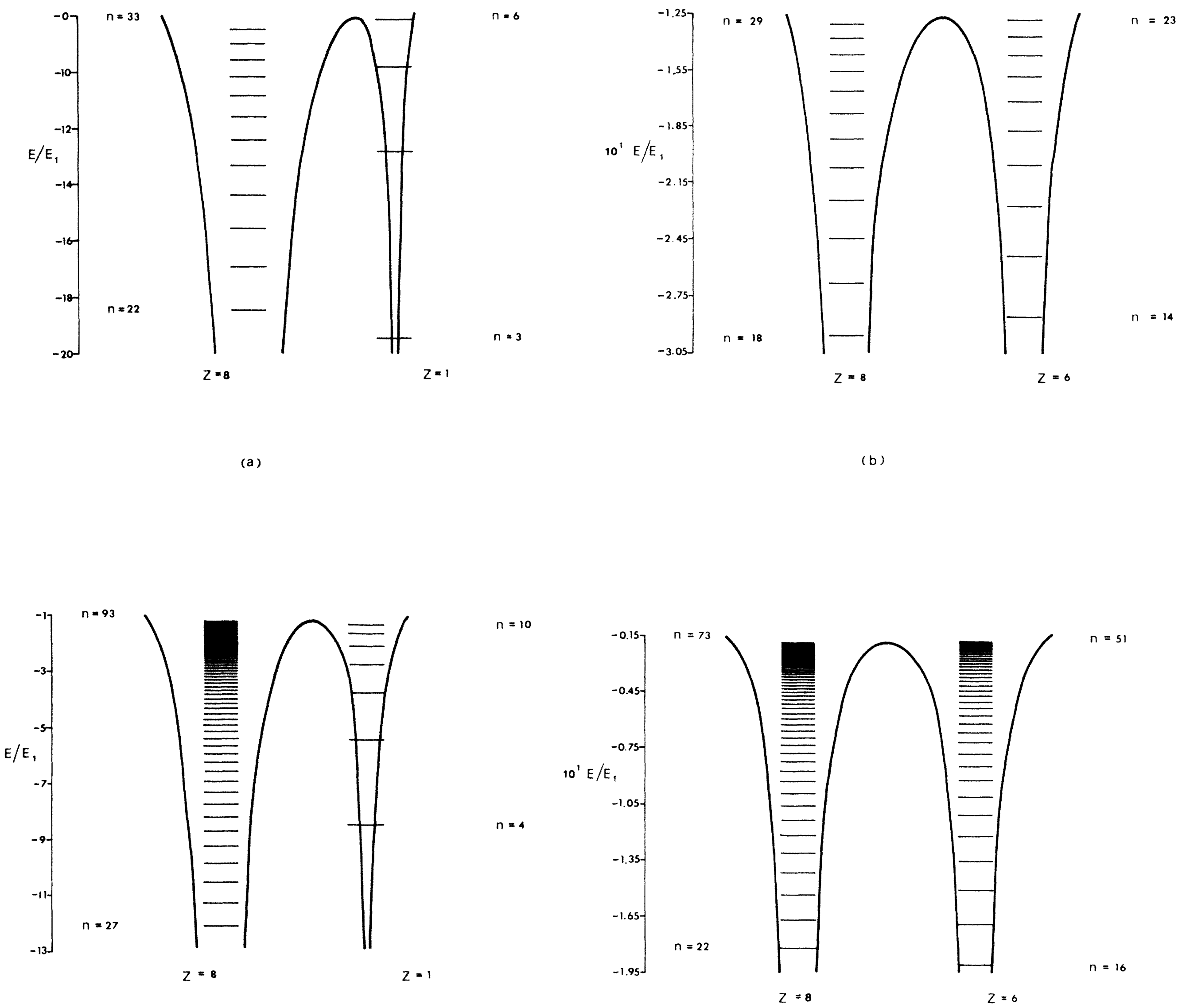

FIG. 7. Atomic states for $V(\mathbf{r}_\pi)$ (upper figure) and $V(\mathbf{r}_\pi)+E_e(\mathbf{r}_\pi)$ (lower figure), in units of E_1: (a) O—H, (b) O—C.

two-center problem without electrons because the potential term in the Hamiltonian is different from that of Eq. (10). Furthermore, the potential E_e is known exactly for a limited number of discrete values only. If spherical symmetry is assumed, as in the preceding section, E_e can be best expressed by a sum of two Yukawa potentials. Unfortunately, a consequence of such a parametrization is that the wave equation can no longer be separated, using confocal elliptic coordinates, thus making the solution very difficult.

An estimation of the change in the pion energy, δW, at internuclear separations corresponding to the bond lengths of the two-center systems can be found by using first-order perturbation theory. If E_e is considered as a small perturbation, then δW is given by

$$\delta W = \int d\tau_\pi |\psi_\pi|^2 E_e , \tag{45}$$

where E_e can be written as the difference between the

TABLE XI. Energies in eV for low-lying $K=0$ states in the H_2 molecule calculated in various potentials. The barrier height without electrons is -77.63 eV and the barrier height with electrons is -29.24 eV.

N	$1/r$ potential without electrons	$1/r$ potential with electrons	Yukawa potential with electrons
1	−3476.98	−3457.39	−3420.85
2	−883.76	−864.36	−827.73
3	−403.54	−384.17	−348.45
4	−235.46	−216.09	−181.38
5	−157.67	−138.30	−104.76
6	−115.41	−96.04	−63.88
7	−89.93	−70.56	−39.95
8	−73.39	−54.02	−25.11
9		−42.68	−15.57
10		−34.57	
11		−28.57	

parametrized form of $(V+E_e)$ and the Coulomb potentials (using parameters obtained in mesoatomic units), i.e.,

$$E_e = -(Z_1/r_1)\exp(-Ar_1) -(Z_2/r_2)\exp(-Br_2) - V(r_\pi) \ . \tag{46}$$

The assumption that E_e is a small perturbation is strictly not valid, except close to the centers. However, the calculation of δW can give some indication of the effect of the electrons on the pion energy. A few calculations are listed in Table XII. The solutions described in Sec. II J were used as the zeroth-order wave functions.

It can be seen from Table XII that the lower quantum states have binding energies (i.e., zeroth-order energies) which are at least an order of magnitude greater than δW. In contrast, the higher states have binding energies which are comparable to, or even less than, the energy change δW. For the latter states, the potential E_e is not a small perturbation and a higher-order calculation is required for a good approximation to the total energy. Thus the calculations without electrons do not give any useful information about pion states with $N \gtrsim 15$.

G. Hydrogen transfer

In the model developed by Ponomarev and coworkers[2–5] it is assumed that pion capture on hydrogen can proceed only through the intermediate stage of a pion molecular orbit. This assumption is based on theoretical calculations for atomic hydrogen[38] which show that the radiative capture rate for muons is very small (10^6–10^7 s^{-1}) compared with the Auger rate (10^{10} s^{-1} for $n=5$). Hence, if the electron is lost, direct atomic capture can proceed only by the slow radiative transitions which are negligible compared with the rate for transitions from a molecular state to an atomic state which is estimated[39] to be $\sim 10^{10} Z^2$ s^{-1}. When, however, the hydrogen atom is one of the molecular systems discussed here, all the valence electrons of the whole molecule are available for refilling.

We have shown that the correct calculation with the inclusion of electrons provides many more atomic states in pionic hydrogen. It can be seen fom Fig. 7 that the density of states in the heavier nucleus near to the top of the barrier is such that unidirectional barrier penetration is a very likely process. The small discrepancies in energy between adjacent states in hydrogen and in the heavier atom are very much less than the vibrational energies, so we can easily anticipate that in the vibrating system exact energy matching can occur.

The highest states in hydrogen are close to the top of the barrier. This means that the exponential factor in a quasiclassical calculation of the barrier penetration will be close to unity and the transition rate for hydrogen transfer depends on the classical frequency with which the pion approaches the barrier. We can estimate the latter from the kinetic energy of the pion, assuming circular orbits, or from the vibrational frequency, and obtain an estimate of the hydrogen transfer rate as 10^{12}–10^{15} s^{-1}. This is quite comparable with typical Auger, radiative, and refilling rates in light atoms,[36,37,40] but much bigger than the radiative rate in atomic hydrogen. Hence the hydrogen transfer process is fast and will dominate over radiative transitions in hydrogen. Even transfer from lower-lying hydrogen states, for which the exponential factor may reduce the transition rate by a few orders of magnitude, will be competitive with radiative transitions.

It may be noted that the pion transferred from hydrogen goes into a state in the heavier atom with a much higher principal quantum number, but with the same energy. There is no obvious mechanism which would cause the orbital angular momentum to change. Hence the transfer process will populate preferentially the lower angular momentum states and this may explain the need[41] for an upper cutoff in the angular momentum distribution chosen to initiate cascade calculations, at least for the kind of molecular system we are discussing here.

It should be noted that our approach to hydrogen transfer is very close in theoretical principle to the explanation given in terms of quasicrossings by Gershtein and Ponomarev.[3,20] Indeed, Gershtein[21] has used this approach for a calculation of the transfer of a muon in a K orbit of hydrogen to a nucleus $Z > 1$. Unfortunately, this

TABLE XII. Results from the perturbation calculations.

Bond	Molecule	R (in units of a_π)	n	l	m	E_{binding} (in units of W_π)	δW (in units of W_π)
H—H	H_2	357	10	0	0	-7.058×10^{-3}	7.487×10^{-3}
			1	0	0	-0.502	7.772×10^{-3}
C—H	CH_4	558	30	0	0	-2.273×10^{-2}	4.664×10^{-2}
			20	0	0	-4.654×10^{-2}	4.713×10^{-2}
			10	0	0	-0.182	4.758×10^{-2}
N—H	NH_3	518	30	0	0	-3.059×10^{-2}	5.719×10^{-2}
			20	0	0	-6.292×10^{-2}	5.77×10^{-2}
			10	0	0	-0.247	5.823×10^{-2}
O—H	H_2O	490	30	0	0	-3.710×10^{-2}	6.894×10^{-2}
			20	0	0	-8.178×10^{-2}	6.958×10^{-2}
			10	0	0	-0.322	7.018×10^{-2}
O—C	CO_2	596	30	0	0	-4.612×10^{-2}	5.110×10^{-2}
			20	0	0	-9.77×10^{-2}	5.283×10^{-2}
			10	0	0	-0.330	5.560×10^{-2}

calculation and others[3,20] use the two-center model without including the molecular electrons.

IV. DISCUSSION AND CONCLUSIONS

We have shown that it is possible to calculate pion molecular eigenenergies and wave functions using codes originally developed to investigate one-electron, two-center problems. As might be expected, the codes were more accurate and efficient at the small internuclear separations and low quantum numbers for which they were originally written. They required greater care when used for pion systems, especially in the case of nonidentical nuclei where quasicrossings were a potential source of error. The problem of quasicrossings was most severe for the higher quantum states, where the energy separation between levels becomes very small.

Bonding pionic states were found only for homonuclear systems. The lack of bonding states for heteronuclear systems does not exclude the formation of molecular orbitals, which by definition only require an energy above the top of the barrier. It does suggest that the pion wave function is centered on one of the two nuclei, usually the heavier of the two. However, the extent of the wave functions for some of he heteronuclear systems is sufficiently large to contribute an important pion density in the region of the lighter nucleus.

Inclusion of the electrons associated with the molecular bonds has proved very significant. The Gaussian basis set used to generate electron wave functions was very useful, as the tables of coefficients and exponents covered an extensive range of molecules. The main disadvantage was that the wave functions are tabulated only for a fixed bond length, which restricted the calculation of the pion-electron potential to one value of the separation between the two centers.

The plots of the pion-electron potential show clearly that the magnitude of E_e is comparable with the pion-nuclear potential in all space, except very close to the nuclear positions. The pion-electron potential for the two-center systems with significantly different nuclei (C—H), N—H, O—H) show that the potential due to the hydrogen atom is dwarfed by the potential due to the heavier atom. For these systems, the pion-nuclear potential along the bond axis is essentially asymmetric between the two centers. However, addition of the two potentials, $V+E_e$, results in a more symmetric total potential.

Because of the importance of E_e away from the nuclear centers, there is a very substantial change in the energies of the pion states for $N>15$. This means that the calculation without electrons does not give any useful information about the pion molecular states for $N \gtrsim 15$.

Another important consequence of adding the pion-electron potential is the substantial increase in the barrier height of the total potential. The energy range available for the formation of molecular orbitals is thus greatly reduced, and the formation of atomic levels close to the top of the barrier becomes more important. Indeed, we may question whether the concept of atomic bound states near the top of the barrier has much meaning and whether either of the formulas for n_0 are significant.

The probability of barrier penetration and transfer fom one of the pionic hydrogen states to a state of corresponding energy in the neighboring heavier atom is greatly enhanced. Clearly, the tunneling process in bonds containing hydrogen is unidirectional. For the O—C bond, however, the density of atomic states for the two centers is not very different and the net effect of transfer should be small.

We conclude that (i) the formation of molecular orbitals is probably less important than is usually implied by the mesomolecular model, (ii) the assumption of direct atomic capture on to hydrogen is justified, and (iii) the tunneling mechanism can explain the transfer of pions from hydrogen to heavier atoms in the same molecule.

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