

# Asymptotic behavior of electron wave functions of polyatomic molecules. Benzene

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A method is proposed for investigating the asymptotic behavior of the wave functions of polyatomic molecules for the case in which the depth of the tunneling penetration of one of the electrons into the sub-barrier region appreciably exceeds the damping radius of the wave function but is comparable with the molecular diameter. The results of an actual calculation for the  $C_6H_6$  molecule are given. It is shown that the asymptotic behavior of the wave function can be represented in the form of a molecular orbital formed from diffuse atomic orbitals, the parameters of which are taken from the calculation. © 1996 American Institute of Physics. [S1063-7761(96)00301-6]

## 1. INTRODUCTION

The present paper is a continuation of investigations into the asymptotic behavior of many-electron wave functions.<sup>1–3</sup> We study the asymptotic behavior of the wave functions  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  of polyatomic molecules (actual calculations are made for benzene) when one of the electrons is outside the main electron localization region (MELR) in the classically inaccessible part of space, so that the length  $l$  of tunneling penetration of the electron appreciably exceeds the damping radius  $a$  of the wave function ( $l \gg a$ ).

Penetration of an electron into the sub-barrier asymptotic region is associated with an extensive class of interesting physical processes (charge exchange and spin exchange in collisions in the gas phase, tunneling electron transport in condensed media, in chemical reactions, intermolecular exchange interaction, etc.).

When  $l$  appreciably exceeds the radius  $a_m$  of the atom and molecule, the existing theory makes it possible to determine the asymptotic behavior of the wave function up to an asymptotic coefficient  $C$  that does not depend on the distance  $r$ . For the simplest systems (atoms), this problem was solved in stages in Refs. 4–9. In Ref. 10, the coefficient  $C$  was determined by the matching method. A more correct method of determining this coefficient is given in Refs. 2 and 3.

For polyatomic molecules, which are considered in the present paper, fundamentally new problems arise, since here the depth  $l$  of tunneling penetration of an electron into the asymptotic region ( $l \gg a_m$ ) can be of the order of or even less than the radius  $a_m$  of the molecule itself ( $l \leq a_m$ ), and the asymptotic methods (including the matching method) developed for the region  $l \gg a_m$  fail completely. It should be noted that even in the case  $l \leq a_m$  the asymptotic values of the molecular wave functions cannot be obtained by means of any quantum-chemical calculation using a variational principle. The contribution of the asymptotic region to the energy of the system is exponentially small, and no modern computer can guarantee such an accuracy of calculation of a many-electron wave function that it corresponds to the contribution of the asymptotic region.

In this paper, the posed problem is solved in the framework of the approach proposed in Ref. 1 based on use of the

Lippmann–Schwinger integral equation. This method makes it possible to construct the asymptotic behavior of the wave function without recourse to matching, using information on the many-electron wave function in the main electron localization region obtained by ordinary quantum-chemical methods, and calculation of the single-electron Green's function for the asymptotic region (with preliminary determination of the effective tunneling potential). Moreover, in our approach it is possible when determining the Green's function to avoid the typical difficulties associated with a semiclassical treatment in the multidimensional case.

## 2. METHOD OF CALCULATION

A general method for obtaining the asymptotic values of many-electron wave functions was proposed in Ref. 1. For completeness of the exposition, we give some general expressions from Ref. 1.

We represent the Hamiltonian  $\hat{H}$  of the  $N$ -electron system in the form ( $e = \hbar = \mu_e = 1$ )

$$\hat{H} = H_0 + U_1 - V_1, \quad H_0 = T + U_{N-1}(\{\mathbf{r}_{N-1}\}) + V(\mathbf{r}_1). \quad (1)$$

Here  $T$  is kinetic-energy operator,  $U_{N-1}(\{\mathbf{r}_{N-1}\})$  is the potential energy of all the electrons except the first ( $\{\mathbf{r}_{N-1}\}$  denotes the set of coordinates  $\mathbf{r}_2, \dots, \mathbf{r}_N$ ), and

$$U_1 = - \sum_k \frac{Z_k}{|\mathbf{r}_1 - \mathbf{R}_k|} + \sum_{m=i}^N \frac{1}{|\mathbf{r}_1 - \mathbf{r}_m|}, \quad (2)$$

where  $\mathbf{R}_k$  is the coordinate of nucleus  $k$ , and  $Z_k$  is its charge. The single-electron potential  $V(\mathbf{r}_1)$  and the method of its determination will be given below.

We investigate the many-electron wave function  $\Psi(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}; E)$  for the case in which one electron is in the deep sub-barrier region and the remainder are in the main region of motion. By means of the Lippmann–Schwinger equation, we can establish the relationship between the required asymptotic behavior of the function  $\Psi(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}; E)$  and its value in the main electron localization region:

$$\Psi(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}; E) = \int d\mathbf{r}'_1 d\{\mathbf{r}'_{N-1}\} G(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}, \mathbf{r}'_1, \{\mathbf{r}'_{N-1}\}) \times (U_1 - V) \Psi(\mathbf{r}'_1, \{\mathbf{r}'_{N-1}\}; E). \quad (3)$$

Here  $G = (E - H_0)^{-1}$  is the Green's function for the Hamiltonian  $H_0$  at given energy  $E$ .

Because the interaction between the first electron and the remaining electrons of the system has been eliminated from  $H_0$ , we can use the following representation for the Green's function  $G$ :

$$G = \sum_{\nu} \varphi_{\nu}(\{\mathbf{r}_{N-1}\}) \varphi_{\nu}^*(\{\mathbf{r}'_{N-1}\}) G_1(\mathbf{r}_1, \mathbf{r}'_1; E - E_{\nu}), \quad (4)$$

where  $\varphi_{\nu}$  and  $E_{\nu}$  are the eigenfunctions and eigenvalues of the  $(N-1)$ -electron Hamiltonian ( $\nu$  is the set of corresponding quantum numbers), and  $G_1$  is the single-particle Green's function at energy  $E - E_{\nu}$  for the Hamiltonian  $\hat{H}_1 = -(1/2)\nabla^2 + V(\mathbf{r}_1)$ .

Substitution of (4) into (3) gives

$$\Psi(\mathbf{r}_1 \rightarrow \infty; \{\mathbf{r}_{N-1}\}; E) = \sum_{\nu} \psi_{\nu}^a(\mathbf{r}_1) \varphi_{\nu}(\{\mathbf{r}_{N-1}\}), \quad (5)$$

where

$$\psi_{\nu}^a = \int d\mathbf{r}'_1 G_1(\mathbf{r}_1, \mathbf{r}'_1; E - E_{\nu}) \int d\mathbf{r}'_{N-1} \varphi_{\nu}^*(\mathbf{r}'_{N-1}) (U_1 - V_1) \psi(\mathbf{r}'_1, \{\mathbf{r}'_{N-1}\}; E). \quad (6)$$

The wave functions  $\psi(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}; E)$ ,  $\varphi_{\nu}(\{\mathbf{r}_{N-1}\})$  are assumed to be symmetrized in the usual manner, since they are the eigenfunctions of Hamiltonians that are symmetric with respect to the interchange of any two electrons. However, since the Hamiltonian  $H_0$  is not symmetric with respect to interchange of the first electron with any other electron, the function  $\Psi(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}; E)$  on the left-hand side of (3) is not symmetric with respect to the interchange  $\mathbf{r} \leftrightarrow \{\mathbf{r}_{N-1}\}$ . This symmetrization procedure must be done additionally.

In accordance with (5), the asymptotic behavior of the wave function of the  $N$ -electron system can be expressed in terms of a superposition of expressions corresponding to the contribution of the different states of the molecular ion (a system of  $N-1$  electrons). The main contribution to the integrals over  $\{\mathbf{r}'_{N-1}\}$  in (6) is made by the main electron localization region. If the wave functions  $\psi(\{\mathbf{r}'_N\})$  and  $\varphi_{\nu}(\{\mathbf{r}'_{N-1}\})$  in this region are calculated to a certain accuracy, it can be assumed that the integrals over  $\{\mathbf{r}'_{N-1}\}$  are calculated to the same accuracy. By the accuracy of  $\psi$  in the main electron localization region we mean a certain overall accuracy, namely, the accuracy of the energy value. As can be seen from (6), the asymptotic behavior is determined by the integral of the wave function calculated in this region. Although the integrals for the determination of the energy are not equal to the integral in (6), we do have such a total accuracy in mind when we speak of the accuracy with which the asymptotic behavior is calculated.

It is convenient to choose the potential  $V_{\nu}$  in the form

$$V_{\nu} = \begin{cases} 0, & \mathbf{r}_1 \in \text{MELR}, \\ \sum_{\mu} \frac{U_{\nu\mu} \psi_{\mu}^a}{\psi_{\nu}^a}, & \mathbf{r}_1 \notin \text{MELR}. \end{cases} \quad (7)$$

It is readily seen that if the expression (7) for  $V_{\nu}$  is substituted into Eq. (6) for  $\psi_{\nu}^a$ , then the integration over  $r'_1$  on the right-hand side of (6) will also be over the main electron localization region. However, since in this region the  $N$ -electron wave function is assumed to be known from quantum-chemical calculations, the choice (7) transforms Eq. (6) into an expression for the asymptotic value of the wave function.

### 3. ITERATIVE PROCEDURE

It can be seen from the expression (7) that the effective tunneling potential  $V$  is found in terms of the asymptotic coefficients of the wave function, which in turn depend on this potential. This means that it is here necessary to use an iterative procedure, the essence of which is presented below. We note first that the calculated effective tunneling potential even at the boundary of the main electron localization region is appreciably smaller than the ionization potential  $I$ . The effective tunneling potential occurs in the definition of the exponent  $\chi$  in the Green's function  $G$ , which can be approximately written in the form

$$\chi = \int_{r'_1}^{r_1} \sqrt{2(I + V(\mathbf{r}'))} dr', \quad (8)$$

where the integration is over the classical trajectory (see below). Under the condition  $V < I$ ,  $V(\mathbf{r}) \rightarrow 0$  as  $\mathbf{r} \rightarrow \infty$ , the potential  $V(\mathbf{r})$  determines the preexponential expression in the Green's function and, therefore, the preexponential expression in the asymptotic behavior  $\psi^a$ . Therefore, the iterative procedure actually amounts to calculation of the preexponential factor, and it is precisely this that is the main task in finding the asymptotic behavior.

We label the states of the ion in order of increasing energy  $E_1 < E_2 < E_3 \dots$  of the ion. In the first iteration (the iterations are labeled with a superscript)

$$V_{\nu}^{(1)} = U_{\nu\nu}, \quad (9)$$

and the  $n$ th iteration gives

$$V_{\nu}^{(n)} = U_{\nu\nu} + \sum_{i \neq \nu} U_{\nu i} \frac{\psi_i^{a(n-1)}(\mathbf{r}_1)}{\psi_{\nu}^{a(n-1)}(\mathbf{r}_1)}, \quad (10)$$

where  $\psi_{\nu}^{a(n)}$  is given by the expression (6), in which  $V_{\nu}^{(n-1)}$  is taken as  $V_{\nu}$ .

The iteration procedure converges if in the given asymptotic region we have

$$|V^{(n)}| < I. \quad (11)$$

For this it is actually sufficient if the inequality (11) holds for  $n=2$ . Calculations show that this iterative procedure converges rapidly (an accuracy  $\approx 1\%$  is guaranteed by the second iteration). However, in the far asymptotic region the inequality (11) can break down. Indeed, the asymptotic behaviors  $\psi_{\nu}^a(r)$  are characterized by different exponential damping radii of the wave functions:

$$\psi_\nu^a(r) \cong \exp\{-\sqrt{2I_\nu}r\}, \quad (12)$$

where  $I_\nu = I + E_\nu$ . Therefore, in the sum on the right-hand side of (10) the terms with  $i < \nu$  at sufficiently large  $r$  are, in general, exponentially growing terms:

$$\frac{\tilde{\psi}_i^a(r)}{\tilde{\psi}_\nu^a(r)} \approx \exp\{[\sqrt{I+E_\nu} - \sqrt{I+E_i}]r\} \quad (E_\nu > E_i).$$

Such growth may lead to the appearance at very large  $r$  of unphysical regions of classically allowed motion of the electron for asymptotic behavior involving excitation of the ion. In this case, the iterative procedure must be modified.

We now turn directly to Eq. (6) and determine the asymptotic behavior  $\psi_i^a$  corresponding to the ground state of the ion in accordance with the prescription described above, i.e., introducing the effective potential  $V_{1(\nu=1)}$  [in accordance with the expression (10)]. Then, using Eq. (6) for the first excited state ( $\nu=2$ ) and separating out the main electron localization region and the asymptotic region (AR), we obtain

$$\begin{aligned} \psi_2^a = & \int_{\text{MELR}} d\mathbf{r}'_1 G_1^{(2)} \int d(\mathbf{r}_{N-1}) \varphi_2^*(U_1 - \tilde{V}_2) \psi \\ & + \int_{\text{AR}} d\mathbf{r}'_1 G_1^{(2)} \int U_{21} \psi_1^a, \end{aligned} \quad (13)$$

where

$$\tilde{V}_2 = \begin{cases} 0, & r_1 \in \text{MELR} \\ \sum_{\mu=2} \frac{U_{2\mu} \psi_\mu^a}{\psi_2^a}, & r_1 \notin \text{MELR}, \end{cases}$$

$$U_{21} = \langle \varphi_2 | U_1 - V_1 | \varphi_1 \rangle = \langle \varphi_2 | U_1 | \varphi_1 \rangle,$$

$$G_1^{(2)} = G_1(\mathbf{r}_1, \mathbf{r}'_1; E - E_2) \quad (14)$$

is the Green's function of the Hamiltonian  $\hat{H} = -(1/2)\nabla^2 + \hat{V}_2(\mathbf{r}_1)$ .

In writing down the second term of (13), we have used the asymptotic behavior of the function  $\psi_1^a$  found from the previous relation of the iterative procedure. It must be emphasized that in the second term of (13) the main contribution is made by the "observation" region  $r_1$ , since when the points  $r'_1$  and  $r_1$  get close to each other the function  $G^{(2)}$  increases more rapidly than the function  $\psi_1^a$  decreases. Thus, the contribution to the far asymptotic behavior from the excited states of the ion can be represented, in general, by two terms,

$$\psi_i^a = a \exp(-\alpha r_1) + b \exp(-\beta r_1), \quad (15)$$

where  $\beta = \sqrt{2I} < \alpha = \sqrt{2(I+E_i)}$  is determined by the ionization potential of the molecule. At the same time, the second term in (15) is of higher order in the small quantity  $r_1$ . Therefore, at finite (but large in the asymptotic sense) values of  $r_1$  the two contributions to the asymptotic behavior of  $\psi_i^a$  may be comparable.

The physical meaning of each term in the far asymptotic region is transparent. Indeed, how can tunneling of an electron with excitation of the ion core occur? First, because of strong interaction within the atom the electron excites the ion

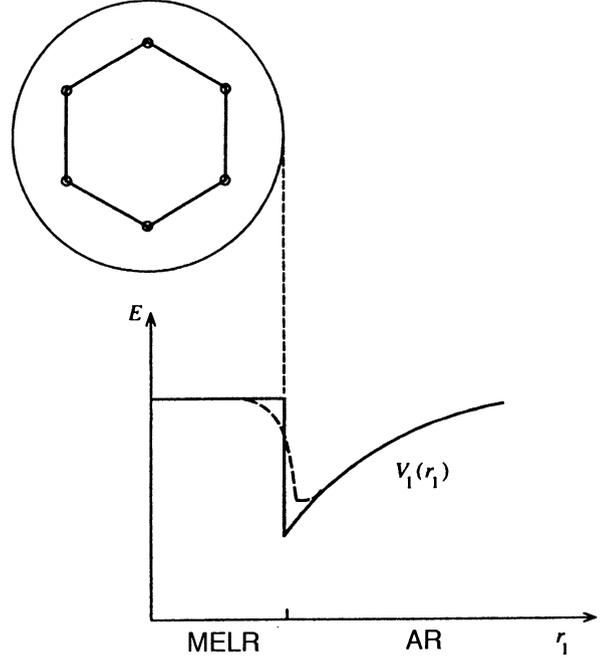


FIG. 1. Schematic representation of the main electron localization region, the asymptotic region, and the effective potential  $V_1$  for the benzene molecule. The dashed curve shows the smoothed boundary of the regions.

core (excitation energy  $E_i$ ) and with energy  $-I - E_i$  goes over into the sub-barrier region. This contribution is described by the first term in (15). Second, the electron tunnels with energy  $-I$  without exciting the ion, and when the "observation" point  $r_1$  is reached, the ion is excited by the multipole interaction ( $U_{21}$ ). This contribution corresponds to the second term in (15). Such a mechanism using a tunneling electron to take energy from the remaining system to realize the most favorable tunneling channel was considered in Ref. 11 for the case of vibronic coupling and in Refs. 12 and 13 for a multipole interelectron interaction.

#### 4. CALCULATION OF THE GREEN'S FUNCTION

As can be seen from (6), to calculate the asymptotic behavior it is necessary to know the single-electron Green's function  $G_1(\mathbf{r}, \mathbf{r}', E)$ . In connection with the special choice of the potential  $V(\mathbf{r}_1)$  (see Fig. 1), for which  $E < V(r_1)$  everywhere, the Green's function can be calculated by a fairly simple semiclassical method. In Ref. 14, for the case in which  $E > V(\mathbf{r}_1)$  in the region of particle motion, the three-dimensional semiclassical Green's function  $G_1(\mathbf{r}, \mathbf{r}', E)$  can be expressed in terms of the action  $S(\mathbf{r}, \mathbf{r}', E)$  along the classical trajectory joining the points  $\mathbf{r}$  and  $\mathbf{r}'$ . The same method can be employed for the sub-barrier case that we consider if the trajectory and action are calculated for an inverted potential in accordance with Ref. 14 ( $V = -V_1$ ,  $E = -E_1$ ). We then obtain

$$G(\mathbf{r}_1, \mathbf{r}'_1) = A(\mathbf{r}_1, \mathbf{r}'_1, E) \exp[-S(\mathbf{r}_1, \mathbf{r}'_1, E)], \quad (16)$$

where

$$A = \frac{1}{4\pi} \left[ \frac{D}{[V(\mathbf{r}_1) - E][V(\mathbf{r}'_1) - E]} \right]^{1/2} \quad (17)$$

( $D$  is the fourth-order determinant formed from the first and second derivatives of  $S$  with respect to the coordinates  $\mathbf{r}_1$  and  $\mathbf{r}'_1$ ). For convenience in the numerical calculation, the step potential  $V$  was smoothed.

The mathematical details of the calculation of the Green's function are given in the Appendix. We merely mention that comparison of the calculated semiclassical Green's function with the known analytic results for the cases ( $V=0$ ,  $V=Fz$ ,  $V=-1/r$ ) in which the semiclassical treatment is valid gives differences of a few percent.

## 5. PROCEDURE FOR CALCULATING THE ASYMPTOTIC BEHAVIOR FOR $C_6H_6$

To calculate the asymptotic behavior, we must have at our disposal wave functions of the molecule and ion calculated by the quantum-chemical method that are sufficiently accurate in the main electron localization region. In the first stage of the calculation, these functions are used to determine effective potentials in accordance with the expression (9). It is then necessary to calculate the Green's function in accordance with the expressions (16) and (17) and determine the asymptotic behavior from the expression (6). In accordance with (10), in the second stage we correct the expressions for the effective potential and repeat the computational procedure described above, etc. In practice, two stages are sufficient.

The main contribution to the asymptotic behavior is made by the most weakly bound  $\pi$ -electron molecular orbitals. The strongly bound filled  $\sigma$  orbitals are taken into account in the effective charges of the ionic cores. The wave functions of the  $C_6H_6$  molecule and the  $C_6H_6^+$  ion in the main electron localization region were calculated by means of the semiempirical CNDO/S and AM1 methods and the nonempirical STO-3G method. The main electron localization region was chosen to be a sphere. The Lippmann-Schwinger equation (6) is invariant with respect to the choice of  $V(\mathbf{r}_1)$ . In accordance with the definition of  $V(\mathbf{r}_1)$ , the expression for the asymptotic behavior of the wave function (7) must be invariant with respect to the choice of the radius of the main electron localization region and of the smoothing potential introduced for numerical convenience (see below). However, this invariance is observed if one uses as  $\psi(\mathbf{r}_1, \{\mathbf{r}_{N-1}\})$  in the integrand on the right-hand side of (6) the exact eigenfunction of the Schrödinger equation and the exact Green's function  $G_1(\mathbf{r}_1, \mathbf{r}'_1; E - E_\nu)$ . In reality, these functions are approximate. Therefore, one must expect that the results of the calculations will depend on the choice of the radius  $r_0$  of the sphere of the main electron localization region. We carried out calculations for  $r_0=6.0$  and  $r_0=6.5$  a.u. The average difference of the asymptotic coefficients was found to be about 4% and the maximum difference 9%. The once-determined wave functions of the molecule and ion were constructed on the same basis of molecular orbitals, and the positions of the nuclei—at the vertices of regular hexagons—were assumed to be the same in the molecule and the ion. The effects associated with the change in the geometry as a result of tun-

neling were not taken into account, since it is precisely in such a (Frank-Condon) approximation that one considers processes associated with fairly rapid removal of the electron (photoelectron transitions, tunneling, etc.).

In accordance with expressions (7) and (9), we obtain for the potential  $V_1$  in the first iteration the expression

$$V_1(\mathbf{r}_1) = \int U(\mathbf{r}_1, \{\mathbf{r}_{N-1}\}) \varphi^2(\{\mathbf{r}_{N-1}\}) d\{\mathbf{r}_{N-1}\}. \quad (18)$$

To high accuracy, this expression can be replaced by the simpler

$$V_1(\mathbf{r}_1) = \sum_i \frac{q_{i\nu}}{|\mathbf{r}_1 - \mathbf{R}_i|}, \quad (19)$$

where  $\mathbf{R}_i$  are the coordinates of the carbon nuclei  $i=1, 2, \dots, 6$ , and  $q_{i\nu}$  is the effective charge at the  $C_i$  atoms in the ionic state  $\nu_i$ . Comparison of  $V_1(\mathbf{r}_1)$  calculated in accordance with the expressions (18) and (19) gives a maximum difference of 4% near the boundary of the main electron localization region. The possibility of using (19) in place of (18) is due to the presence of an uncompensated electric charge in our system. Compared with its field, the corrections due to allowance for the distribution of the electron density in each atomic orbital are negligible, and the corrections from the nonuniform distribution of the positive charge over the carbon atoms can be taken into account in both expressions. It should be noted that for electrically neutral systems, (18) and (19) give very different results. The potentials  $V_1(\mathbf{r}_1)$  determined in accordance with (18) or (19) using these different quantum-chemical methods of calculating the wave functions in the main electron localization region agree to very high accuracy. Even near the boundary of this region, the differences are less than 1%. This is due to the fact that the coefficients in the expansion of the  $\pi$ -electron molecular orbitals of benzene (and, therefore, the charges on the atoms of the anion) are determined by the symmetry of the molecule and do not depend on the method of calculation. The calculations showed that further iterations of the potential  $V_1(\mathbf{r}_1)$  in accordance with the expression (10) lead to a slight (less than 4%) change in the potential  $V_1(\mathbf{r}_1)$ . When the asymptotic behavior is calculated in accordance with (5) and (6), there arise expressions of the type  $U_{\text{eff}}\varphi_a(\mathbf{r}_1)$ , where  $U_{\text{eff}}$  is the effective self-consistent potential within the molecule that acts on electron 1, and  $\varphi_a(\mathbf{r}_1)$  is the  $a$ th molecular region. This expression can be conveniently replaced:

$$\begin{aligned} U_{\text{eff}}\varphi_a(\mathbf{r}_1) &= \left( -\frac{1}{2} \Delta_{r_1} + U_{\text{eff}}(\mathbf{r}_1) + \frac{1}{2} \Delta_{r_1} \right) \varphi_a(\mathbf{r}_1) \\ &= I_a \varphi_a(\mathbf{r}_1) + \frac{1}{2} \Delta_{r_1} \varphi_a(\mathbf{r}_1), \end{aligned} \quad (20)$$

where  $I_a$  is the ionization potential of an electron from the  $a$ th molecular orbital. The use of (21) greatly simplifies the calculations.

## 6. RESULTS AND DISCUSSION

The asymptotic behavior of the  $C_6H_6$  wave functions was calculated in the first iteration for all three  $\pi$ -electron

orbitals of benzene, i.e., for the states of the ion that are characterized by the absence of an electron in the three filled orbitals of the benzene molecule. It was found that the results obtained can be well approximated by an analytic function. We call it the diffuse orbital:

$$\varphi_\nu^{\text{dif}}(\mathbf{r}_1) = a_\nu \sum_i C_{i\nu} \chi_\nu^{\text{dif}}(\mathbf{r}_1 - \mathbf{R}_i). \quad (21)$$

Here  $C_{i\nu}$  are the coefficients in the expansion of the molecular orbitals  $\varphi_\nu$  with respect to the basis of Slater atomic orbitals, and  $\chi_\nu^{\text{dif}}$  is the diffuse atomic orbital:

$$\chi_\nu^{\text{dif}}(\mathbf{r}) = \sqrt{\frac{3}{\pi}} (2I_\nu)^{3/4} \frac{z}{r} \exp(-\sqrt{2I_\nu}r). \quad (22)$$

Here  $I_\nu = I + E_\nu$  is the ionization potential of an electron from the molecular orbital  $\varphi_\nu$ , and  $E_\nu$  is the excitation energy of the ion.

The fitting coefficients  $a_\nu$  are found to have the following values:

$a = 0.12$  for the upper doubly degenerate molecular orbital ( $1e_{1D}$ ),

$a = 0.15$  for the lower completely symmetric molecular orbital ( $1e_{2D}$ ).

The function  $\varphi_\nu^{\text{dif}}(\mathbf{r})$  fits the numerical calculations to an accuracy of about 3%. As we have already noted, subsequent iterations in the calculation of the asymptotic behavior agree with the first iteration to an accuracy of about 4%. Thus, Eqs. (21) and (22) give the expressions for the asymptotic behaviors of the wave functions. However, we emphasize that the coefficient  $a_\nu$  in (21) can be obtained only by numerical calculation. The calculated molecular orbital (the wave function within the main electron localization region) and the diffuse molecular orbital (the wave function in the asymptotic region) have the same angular dependence, this being due to the high symmetry of the benzene molecule.

Figure 2 shows  $|\psi_\nu(r, \varphi, \theta)|$  in the main electron localization region and in the asymptotic region, where  $\theta$  is the angle measured from the axis  $C_6$ , and the angle  $\varphi$  corresponds to the direction to the C atom with the largest coefficient of the  $\pi$  orbital. To the accuracy of the calculation, the values of  $\psi_\nu^{\text{dif}}$  and  $\psi_\nu$  are the same on the boundary of the main electron localization region at the point  $r_0$ . It can be clearly seen in the figure that simple asymptotic continuation of  $\psi_\nu$  beyond the main electron localization region is absolutely incorrect.

#### APPENDIX: ALGORITHM FOR NUMERICAL CALCULATION OF THE GREEN'S FUNCTION

In the semiclassical approximation, the Green's function  $G(r_0, r_k)$  is given by the expression (16), in which  $S(r_0, r_k)$  is the action calculated along the extremal trajectory corresponding to the given energy level  $E_0$ :

$$S(r_0, r_k) = \int_{r_0}^{r_k} \sqrt{2[E - V(z)]} dz. \quad (A1)$$

The extremal trajectory  $[x_1(t), x_2(t), x_3(t)]$  along which the action (A1) is calculated is determined from the system of nonlinear equations

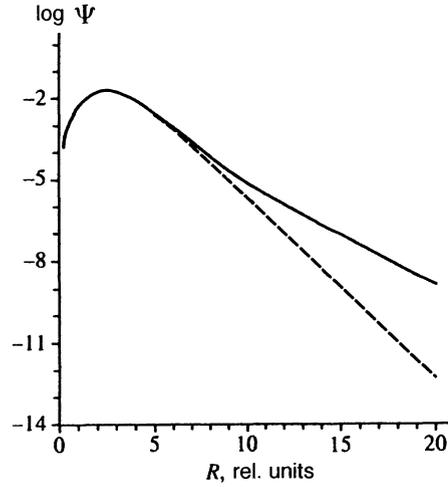


FIG. 2. Radial dependence of the wave function of the upper occupied molecular orbital of benzene. The continuous curve is calculated with Slater orbitals within the main electron localization region in accordance with the theory presented in the present paper. Outside this region, the dashed curve gives the result of the calculation with Slater orbitals;  $R$  is measured from the center of the molecule.

$$\ddot{x}_i + \frac{\partial V}{\partial x_i} = 0, \quad i = 1, 2, 3, \quad (A2)$$

with given  $(x_1^0, x_2^0, x_3^0)$  and  $(x_1^k, x_2^k, x_3^k)$ . This is a problem with time as a free parameter, and the extremal trajectory belongs to the given energy level  $E_0$  and ensures a minimum of the functional (A1). Thus, to calculate the Green's function it is necessary to find the extremal trajectory of the variational problem (A1), (A2) belonging to the given energy level  $E_0$  and then calculate along the optimum trajectory the derivatives of the action with respect to the initial and final points; these occur in the preexponential factor of the expression (16).

For our calculations, it proved to be more convenient to consider a different variational problem, which is equivalent to the one posed above. Namely, consider the functional

$$S = \int_0^T \left( \frac{1}{2} (\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2) - V(\mathbf{r}) + E \right) dt, \quad (A3)$$

in which the time  $T$  is also regarded as a free parameter, and the extremum belongs to the given energy level  $E_0$ . It is obvious that in this case the extremal trajectory satisfies the same system of equations (A2). It can be shown that the action calculated along the extremum in accordance with (A1) and (A3) will be the same.

We assume that the original trajectory is determined over the interval  $[0, T]$ . We make the change of variables  $\tau = t/T$ ,  $\tau \in [0, 1]$ . Then Eqs. (A2), (A3) can be rewritten in the form

$$\frac{1}{T^2} \ddot{x}_i + \frac{\partial V}{\partial x_i} = 0, \quad i = 1, 2, 3, \quad (A4)$$

$$S = \int_0^1 \left( \frac{1}{2T^2} (\dot{x}_1^2 + \dot{x}_2^2 + \dot{x}_3^2) - V + E \right) dt. \quad (A5)$$

We specify a certain number  $T$  and solve the boundary-value problem (A4). The solution we find—if it exists—will correspond to a certain value  $E(T)$  of the energy that, in general, is different from  $E_0$ . Solving then the equation

$$E(T) = E_0, \quad (\text{A6})$$

we find the value of  $T_0$  for which the resulting solution will belong to the necessary level  $E_0$ . We emphasize that to calculate one value of the function  $E(T)$  in (A6) it is necessary to solve a boundary-value problem for the system of nonlinear equations (A4). This boundary-value problem was solved by the method of stabilization, i.e., the solution of the stationary problem was obtained as the limit with respect to a formally introduced time  $\tau'$  of the solution of the nonstationary problem. In such an approach, the integration step size in the artificially introduced time  $\tau'$  can be regarded as a formal iteration parameter. The corresponding nonstationary problem was solved by the method of finite differences with approximation of the spatial derivatives from the upper layer and with the use of complete linearization of the nonlinear terms. We mention that for sufficiently small value of  $E_0$  (below the barrier) the iterative process will not converge, since in this case the original trajectory does not exist. The higher the level  $E_0$  (but necessarily above the barrier), the more rapidly the iteration process converges.

To calculate the preexponential factor in the expression for the Green's function, it is necessary to vary the problem in the neighborhood of the obtained trajectory with respect to the boundary conditions  $(x_1^0, x_2^0, x_3^0)$  and  $(x_1^k, x_2^k, x_3^k)$ . The necessary first and second derivatives of the action with respect to the initial and final points will be expressed in terms of the solution of the resulting linearized system.

Omitting the calculations, we give the final result:

$$\frac{\partial S}{\partial x_i^k} = \frac{1}{T_0} \dot{x}_i(1), \quad \frac{\partial S}{\partial x_i^0} = -\frac{1}{T_0} \dot{x}_i(0), \quad (\text{A7})$$

$$\frac{\partial^2 S}{\partial x_i^0 \partial x_j^k} = -\frac{1}{T_0} \dot{U}_{ij}(0) - \frac{1}{T_0} \frac{\partial S}{\partial x_i^0} \frac{\partial T_0}{\partial x_j^k}. \quad (\text{A8})$$

Here  $U_{ij}$  is the solution of the linearized system that satisfies the boundary conditions  $U_{ij}(0)=0$ ,  $U_{ij}(1)=\delta_{ij}$ ,  $i, j=1, 2, 3$ . To calculate  $\partial T_0 / \partial x_j^k$  in the expression (A8), we must differentiate the identity

$$\frac{1}{2T_0^2} (x_1^2 + x_2^2 + x_3^2) + V = E.$$

We emphasize that for exact solution of the linearized system the potential  $V$  must have smooth second derivatives.

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