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## Unique Orbitals\*

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A method is presented which allows reduction of exact wave functions of one electron diatomic molecules to "unique" orbitals from which exact wave functions for the particular molecule can be written as LCAO-MO functions. The method is illustrated with applications to the hydrogen molecule-ion and the doubly charged helium hydride molecule-ion. Extension of the method to two electron "unique" geminals is discussed.

On présente une méthode qui permet la réduction des fonctions d'onde exactes de n'importe quelle molécule diatomique monoélectronique aux orbitales «*uniques*», sur base desquels les fonctions exactes des molécules s'écrivent en combinaisons linéaires. La méthode est illustrée par les exemples de  $H_2^+$  et  $HeH^{++}$ . On discute son extension sur des géminaux «*uniques*» d'électrons.

Ein Verfahren wird angegeben, aus exakten Eigenfunktionen zweiatomiger Moleküle mit einem Elektron „*unique*“ = einzigartige Orbitale zu gewinnen, aus denen sich die exakten Molekülfunktionen als Linearkombinationen ergeben. Anwendungen auf  $H_2^+$  und  $HeH^{++}$  erläutern die Methode. Die Erweiterung auf „*unique*“-Elektronengeminale wird diskutiert.

### Introduction

One of the most commonly used methods of forming molecular wave functions is the LCAO-MO (molecular orbital formed as a linear combination of atomic orbitals) method. This method is very useful conceptually in that it allows a physical significance to be attributed to the function and its constituent atomic orbitals. Unfortunately the most accurate molecular wave functions are not of this form but are usually complicated solutions to differential equations [1, 2] or, are in the form of power series times exponentials [4]. The physical meaning of these complicated wave functions is not easy to visualize since the familiar concept of atomic orbitals is not applicable to them.

In the following section a method is presented which allows the reduction of exact wave functions for one electron diatomic molecules to "unique" orbitals from which exact wave functions for the particular molecule can be written as LCAO-MO functions.

Applications are given to the hydrogen molecule-ion and the doubly charged helium hydride molecule-ion.

### Unique Orbitals

The set of "unique" orbitals for a particular molecule can be considered as consisting of pairs of orbitals; one,  $\Psi_a$ , centered about nucleus  $a$ , and the other,

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$\Psi_b$ , about nucleus  $b$ . The orbitals are to be constructed such that the exact molecular wave function,  $\Psi$ , may be written as

$$\Psi = \Psi_a + c \Psi_b \quad (1)$$

where  $c$  is equal to  $\pm 1$  for the homonuclear case and none of the wave functions are necessarily normalized.

There are an infinite number of ways by which one might form a set of orbitals that would satisfy (1), but few that would give the derived functions the properties that one would expect of an atomic orbital such as going to zero smoothly as the electron goes to infinity and "cusps" (i. e., point of discontinuity in the first derivative) appearing only at the nucleus about which the function is centered. Cusps can occur only for  $\sigma$  orbitals since otherwise  $\Psi = 0$  at each nucleus.

A unique set of orbitals with the desired properties can be derived as follows. Consider the Hamiltonian operator,  $\mathcal{H}$ , as being divided into two parts,  $T$  and  $V$ ;  $T$  representing kinetic energy and  $V$  potential energy. Then for any eigenfunction of the molecule,

$$\begin{aligned} \mathcal{H} \Psi &= E \Psi \\ (T + V) \Psi &= E \Psi \end{aligned} \quad (2)$$

or

$$T \Psi / \Psi = E - V .$$

For a one electron diatomic molecule, in atomic units.

$$V = -\frac{q_a}{r_a} - \frac{q_b}{r_b}$$

$q_a, q_b$  = charges on nuclei  $a$  and  $b$ , respectively.

As  $r_a$  or  $r_b$  goes to zero,  $-V$  goes to infinity and because of this the exact molecular wave function has cusps at both nuclei.

It is suggested that a unique method of forming an orbital,  $\Psi_a$ , centered about nucleus  $a$  would be to require that  $(T \Psi_a / \Psi_a)$  be finite as  $r_b$  goes to zero and, for  $\Psi_b$  require that  $(T \Psi_b / \Psi_b)$  be finite as  $r_a$  goes to zero. Then  $\Psi_a$  and  $\Psi_b$  may have cusps at their respective nuclei but none at the other nucleus in either case and the orbitals will go to zero smoothly as either  $r_a$  or  $r_b$  approaches infinity. This condition on  $T \Psi / \Psi$  is more general than the condition for presence or absence of cusps.

In the following illustrations of the method it is easier to discuss the homonuclear and heteronuclear cases separately.

#### Homonuclear case: Hydrogen molecule-ion

Let  $\Psi_1$  and  $\Psi_2$  be exact bonding and antibonding molecular orbitals, respectively, formed by the LCAO-MO method from the "unique" orbitals  $\Psi_a$  and  $\Psi_b$ ,

$$\begin{aligned} \Psi_1 &= c_1 (\Psi_a + \Psi_b) \\ \Psi_2 &= c_2 (\Psi_a - \Psi_b) . \end{aligned}$$

Then, solving for  $\Psi_a$  and  $\Psi_b$

$$\begin{aligned} \Psi_a &= \frac{1}{2c_1} \Psi_1 + \frac{1}{2c_2} \Psi_2 \\ \Psi_b &= \frac{1}{2c_1} \Psi_1 - \frac{1}{2c_2} \Psi_2 \end{aligned}$$

or, since the functions are not required to be normalized

$$\begin{aligned}\Psi_a &= \Psi_1 + k \Psi_2 \\ \Psi_b &= \Psi_1 - k \Psi_2\end{aligned}\quad (3)$$

where, from above,  $k$  will be determined by requiring

$$[T \Psi_a / \Psi_a]_{r_b=0} = \text{finite} . \quad (4)$$

Since this is a homonuclear molecule,  $k$  is the same for both  $\Psi_a$  and  $\Psi_b$ .

It seems logical that the same rate of exponential fall off should be considered for both parts of a single atomic orbital. The rate of exponential fall off depends on both the exponential parameter and the internuclear distance.

For  $\text{H}_2^+$  the lowest bonding state,  $1s\sigma_g$ , and the lowest antibonding state,  $2p\sigma_u$ , should occur with different exponential parameters [6], and the exponential parameter for the lower state should be larger than that for the upper state. This is easily seen from a consideration of the united atom or the asymptotic solution. If the exact solution is assumed to be of the form [2]

$$\Psi = F(r_a, r_b) \exp[-\alpha(r_a + r_b)] \quad (5)$$

where  $F(r_a, r_b)$  goes to infinity much slower than  $\exp[+\alpha(r_a + r_b)]$ , the limiting behavior is determined by the exponential factor and the asymptotic solution yields, in atomic units,

$$E = -2\alpha^2 . \quad (6)$$

Since  $E_{1s\sigma_g} < E_{2p\sigma_u}$  we have  $\alpha_{1s\sigma_g} > \alpha_{2p\sigma_u}$  and the upper state would trail off more slowly than the lower state if the same internuclear distance was considered for both wave functions.

One method of assuring the same rate of exponential fall off for both functions is to use scaled coordinates. Let

$$x^0 = \zeta x, \quad R^0 = \zeta R, \text{ etc.},$$

where  $x^0$  is a scaled coordinate and  $\zeta$  is a scaling parameter. The scaled unique orbitals can be formed as

$$\begin{aligned}\Psi_a^0 &= \Psi_1^0 + k^0 \Psi_2^0 \\ \Psi_b^0 &= \Psi_1^0 - k^0 \Psi_2^0\end{aligned}\quad (7)$$

where  $\Psi_1^0$  and  $\Psi_2^0$  are eigenfunctions taken at corresponding scaled values of the internuclear distance. That is, if  $R_1$  is the actual internuclear distance of the lower state, the scaled values are

$$R^0 = \zeta_1 R_1 = \zeta_2 R_2 \quad (8)$$

where the most convenient  $\zeta$  to use is the exponential parameter in (5).

In scaled coordinates the Schroedinger equation becomes [5]

$$(\zeta^2 T_0 + \zeta V_0) \Psi^0 = E \Psi^0 ,$$

or, if  $\zeta$  is the exponential parameter in (5) and (6),

$$\left(T_0 + \frac{1}{\zeta} V_0\right) \Psi^0 = \frac{E}{\zeta^2} \Psi^0 = -2 \Psi^0 , \quad (9)$$

where  $T_0$  and  $V_0$  are in terms of scaled coordinates.

The unique orbitals can be determined by requiring  $(T_0 \Psi_a^0 / \Psi_a^0)$  be finite for  $r_b^0 = 0$ . Since  $\Psi_1^0$  and  $\Psi_2^0$  are eigenfunctions for the molecule,

$$\left(T_0 + \frac{1}{\zeta_i} V_0\right) \Psi_i^0 = \frac{E_i}{\zeta_i^2} \Psi_i^0 = -2 \Psi_i^0 ; \quad i = 1, 2$$

and

$$\begin{aligned} \frac{T_0 \Psi_a^0}{\Psi_a^0} &= \frac{-2 \Psi_1^0 - \frac{1}{\zeta_1} V_0 \Psi_1^0 + k^0 \left(-2 \Psi_2^0 - \frac{1}{\zeta_2} V_0 \Psi_2^0\right)}{\Psi_1^0 + k^0 \Psi_2^0} \\ &= -2 - V_0 \frac{\left(\frac{1}{\zeta_1} \Psi_1^0 + k^0 \frac{1}{\zeta_2} \Psi_2^0\right)}{(\Psi_1^0 + k^0 \Psi_2^0)} . \end{aligned} \quad (10)$$

Since  $-V_0$  goes to infinity at  $r_b = 0$  for  $(T_0 \Psi_a^0 / \Psi_a^0)$  to remain finite the coefficient of  $V_0$  must go to zero: therefore if the denominator is not zero the numerator goes to zero and

$$\begin{aligned} \left(\frac{1}{\zeta_1} \Psi_1^0 + k^0 \frac{1}{\zeta_2} \Psi_2^0\right)_{r_b=0} &= 0 \\ k^0 &= -(\zeta_2 \Psi_1^0 / \zeta_1 \Psi_2^0)_{r_b=0} \end{aligned}$$

or, from (8)

$$k^0 = -(R_1 \Psi_1^0 / R_2 \Psi_2^0)_{r_b=0} . \quad (11)$$

Equations (7) and (11) therefore determine unique orbitals, at least to within a normalization constant.

For a molecular orbital other than  $\sigma$  there is a node along the molecular axis and the denominator in (10) is zero. In the wave functions used below the node arises from a factor

$$[(\lambda^2 - 1)(1 - \mu^2)]^{m/2}$$

where  $m = 0, 1, 2, \dots$  for  $\sigma, \pi, \delta \dots$

The molecular orbital without this factor has cusps at the nuclei. This factor cancels out between numerator and denominator in equ. (10) and the resulting equation (11) can then apply to the factored function with cusps.

Note that if we had not determined the scaling parameters from (6) and instead had used unscaled functions at the same internuclear distance ( $\zeta_1 = \zeta_2, R_1 = R_2$ ), equations (7) and (11) force  $\Psi_a$  to have a node at nucleus  $b$ . There is no a priori reason to expect an orbital centered about nucleus  $a$  to have a node at nucleus  $b$  and this can be considered further justification for the use of scaled coordinates.

For these orbitals to be considered a unique set there should be an unambiguous method of choosing the proper wave functions to combine. For the hydrogen molecule-ion this choice can be made through the use of a correlation diagram between states of the united atom and states of the separated atoms [3]. The molecular wave functions were chosen in pairs of bonding and antibonding functions such that both had the same rotational symmetry and both corresponded to the same state of the separated atoms. This leads to the following combinations:

$$ns \sigma_g \text{ with } (n + 1) p \sigma_u ,$$

Table 1

Molecule	Function	$R$	$p$	$\sigma$	$m$	$\zeta$
$H_2^+$	$1s \sigma_g$	2.0	1.48501	0.34679	0	0.74251
	$2p \sigma_u$	2.52344	,,	0.69927	0	0.58849
	$2s \sigma_g$	3.89081	,,	1.62006	0	0.38167
	$3p \sigma_u$	4.26254	,,	1.87038	0	0.34839
	$3s \sigma_g$	5.68954	,,	2.83131	0	0.26101
	$4p \sigma_u$	5.99355	,,	3.03603	0	0.24777
	$2p \pi_u$	3.45542	..	0.32687	1	0.42976
	$3d \pi_g$	4.37074	,,	0.94324	1	0.33976
	$3d \sigma_g$	3.93996	,,	1.65315	0	0.37691
	$4f \sigma_u$	5.56951	,,	2.75049	0	0.26663
$HeH^{++}$	$1s \sigma$	2.0	2.24151	0.33838	0	1.12076
	$2p \sigma$	2.89884	,,	0.93988	0	0.77324

$np \pi_u$  with  $(n + 1) d \pi_g$ ,

and

$nd \sigma_g$  with  $(n + 1) f \sigma_u$ .

The wave functions used were obtained through interpolation in the tables given by BATES, LEDSHAM, and STEWART [2] and the basic parameters and scale factors are given in Tab. 1. The parameters given refer to a wavefunction of the form

$$\Psi(\lambda, \mu, \varphi) = A(\lambda) M(\mu) \Phi(\varphi)$$

where

$$\lambda = \frac{r_a + r_b}{R}, \quad \mu = \frac{r_a - r_b}{R}, \quad \varphi = \text{azimuthal angle};$$

and

$$\begin{aligned} \Phi(\varphi) &= \frac{\cos}{\sin}(m\varphi) \\ A(\lambda) &= (\lambda^2 - 1)^{m/2} (\lambda + 1)^\sigma \exp(-p\lambda) \sum_{t=0}^{\infty} g_t \left(\frac{\lambda - 1}{\lambda + 1}\right)^t \\ M(\mu) &= \sum_s f_s P_{m+s}^m(\mu). \end{aligned} \quad (12)$$

The coefficients  $g_t$  and  $f_s$  are too numerous to tabulate here but are easily obtained through interpolation in the tables given in [2] using the basic parameters given in Tab. 1.

Five sets of unique orbitals for  $H_2^+$  were determined and the constants are given in Tab. 2. To illustrate the shapes of the unique orbitals, Fig. 1 presents a

Table 2

Molecule	Functions combined	$k_H^0$	$k_{He}^0$
$H_2^+$	$1s \sigma_g, 2p \sigma_u$	0.72692	
	$2s \sigma_g, 3p \sigma_u$	0.89710	
	$3s \sigma_g, 4p \sigma_u$	0.96580	
	$2p \pi_u, 3d \pi_g$	0.18378	
	$3d \sigma_g, 4f \sigma_u$	0.30355	
$HeH^{++}$	$1s \sigma, 2p \sigma$	8.4710	0.41605

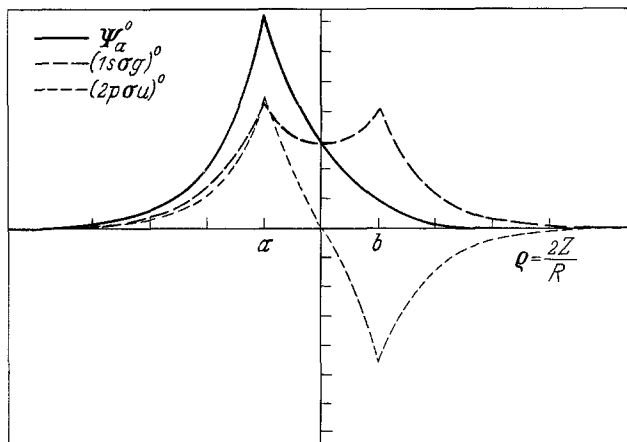


Fig. 1. Molecular Wavefunctions and Unique Orbital for  $H_2^+$ , plotted along the molecular axis

plot of the unique orbital  $\Psi_a^0$  derived from the  $1s\sigma_g$  and  $2p\sigma_u$  states. The functions are plotted along the molecular axis versus the dimensionless parameter  $\rho = 2z/R$ . Fig. 2 shows the same functions plotted perpendicular to the molecular axis at nucleus  $b$  versus  $\rho = 2x/R$ .

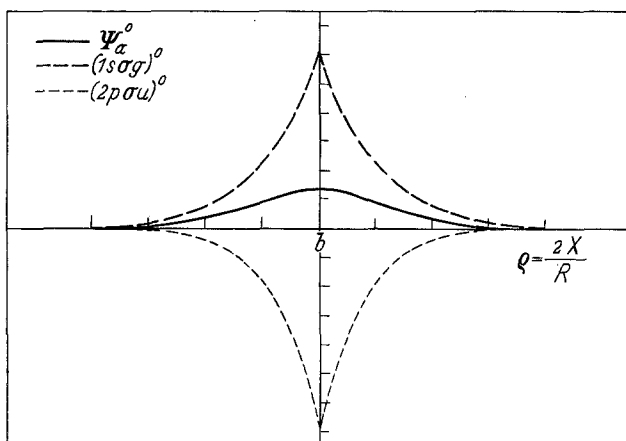


Fig. 2. Molecular Wavefunctions and Unique Orbital for  $H_2^+$ , plotted perpendicular to the molecular axis

### Heteronuclear case: Helium Hydride molecule-ion

For a heteronuclear molecule  $\Psi_a^0$  and  $\Psi_b^0$  will, of course, not be symmetrically related as they are for the homonuclear case. The scaled unique orbitals can be written as

$$\begin{aligned}\Psi_a^0 &= \Psi_1^0 + k_a^0 \Psi_2^0 \\ \Psi_b^0 &= \Psi_1^0 - k_b^0 \Psi_2^0\end{aligned}\quad (13)$$

and the exact molecular functions as (unnormalized)

$$\begin{aligned}\Psi_1^0 &= \Psi_a^0 + \frac{k_a^0}{k_b^0} \Psi_b^0 \\ \Psi_2^0 &= \Psi_a^0 - \Psi_b^0.\end{aligned}$$

From (10) and (11) then,

$$k_a^0 = - \left( \frac{R_1 \Psi_1^0}{R_2 \Psi_2^0} \right)_{r_b^0} = 0$$

$$k_b^0 = \left( \frac{R_1 \Psi_1^0}{R_2 \Psi_2^0} \right)_{r_a^0} = 0 \quad (14)$$

The heteronuclear diatomic molecule has the same types of possible states as the homonuclear diatomic except that the  $g$  or  $u$  property has been lost. Therefore the choice of states to combine corresponds to the homonuclear case:

$$ns \sigma \text{ with } (n + 1) p \sigma,$$

$$np \pi \text{ with } (n + 1) d \pi,$$

and

$$nd \sigma \text{ with } (n + 1) f \sigma.$$

Exact wave functions are available for fewer states of  $\text{HeH}^{++}$  than for  $\text{H}_2^+$ . Unique orbitals were determined for the  $1s \sigma$  and  $2p \sigma$  states utilizing data from the tables of BATES and CARSON [1]. The basic parameters for these wave functions

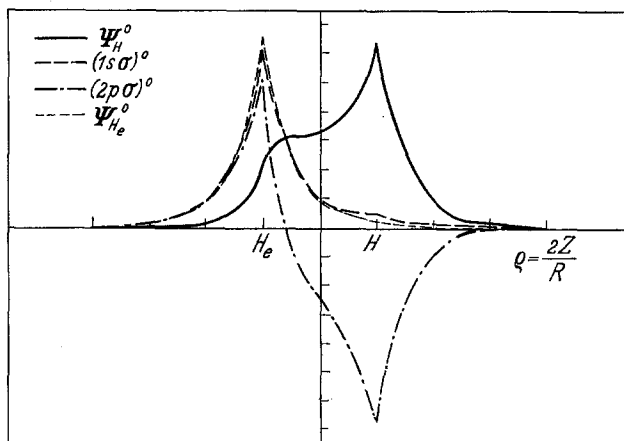


Fig. 3. Molecular Wavefunctions and Unique Orbital for  $\text{HeH}^{++}$ , plotted along the molecular axis. The  $(2p\sigma)^0$  function is increased by a factor of 10

and the unique orbitals are given in Tab. 1 and 2. The functions of BATES and CARSON are the same as (12) except for  $M(\mu)$  and, for the range of internuclear distances considered, it is given by

$$M(\mu) = \exp(-p\mu) \sum_{t=m}^{\infty} f_t' P_t^m(\mu) \quad (15)$$

The expansion coefficients are readily obtained from the tables given in [1] by interpolation using the basic parameters in Tab. 1.

In Fig. 3 the molecular wave functions,  $\Psi_{\text{He}}^0$ , and  $\Psi_{\text{H}}^0$  are plotted along the molecular axis versus  $\rho = 2z/R$ .

### Unique Geminals

For a diatomic molecule, a set of two electron "unique" geminals analogous to the set of "unique" orbitals would be composed of quartets of geminals. The

geminals in a specific quartet would be labeled  $\Psi_{ab}$ ,  $\Psi_{ba}$ ,  $\Psi_{aa}$ , and  $\Psi_{bb}$  where  $\Psi_{\alpha\beta}$  refers to a geminal with electron 1 around nucleus  $\alpha$  and electron 2 around nucleus  $\beta$ .

For the two electron diatomic molecule, in atomic units,

$$V = -\frac{q_a}{r_{a1}} - \frac{q_b}{r_{b1}} - \frac{q_a}{r_{a2}} - \frac{q_b}{r_{b2}} + \frac{1}{r_{12}}$$

and  $V$  becomes infinite if any of the interparticle coordinates goes to zero. In analogy to the one electron case it is suggested that the geminals be formed through the requirement that  $(T \Psi_{\alpha\beta} | \Psi_{\alpha\beta})$  be finite for each of the following functions and its accompanying conditions.

$$\begin{aligned} \text{For } \Psi_{ab} \text{ if } r_{b1} \text{ or } r_{a2} &= 0 \\ \Psi_{ba} \text{ if } r_{a1} \text{ or } r_{b2} &= 0 \\ \Psi_{aa} \text{ if } r_{b1} \text{ or } r_{b2} &= 0 \\ \Psi_{bb} \text{ if } r_{a1} \text{ or } r_{a2} &= 0. \end{aligned}$$

As an example, the four lowest states of the hydrogen molecule could be represented as

$$\begin{aligned} 1\Sigma_g^+ \text{ (ground)} &= c_1 (\Psi_{ab} + \Psi_{ba}) + c_2 (\Psi_{aa} + \Psi_{bb}) \\ 3\Sigma_u^+ &= c_3 (\Psi_{ab} - \Psi_{ba}) \\ 1\Sigma_u^+ &= c_4 (\Psi_{aa} - \Psi_{bb}) \\ 1\Sigma_g^+ \text{ (excited)} &= c_5 (\Psi_{aa} + \Psi_{bb}) - c_6 (\Psi_{ab} + \Psi_{ba}). \end{aligned}$$

Unfortunately, sufficiently accurate wavefunctions for the excited states of the hydrogen molecule have not been determined over the ranges of exponential parameters and internuclear distances that would be required to determine a set of unique geminals for this molecule.

### Conclusion

It has been shown that exact wavefunctions for one electron diatomic molecules can be reduced to a set of "unique" orbitals centered on the two nuclei such that the exact wavefunctions are expressible as LCAO-MO functions of these orbitals. The derived functions have the properties that one normally expects to find in an atomic orbital in that there are cusps only at the nucleus about which the orbital is centered, the orbitals are continuous, and they go smoothly to zero as the electron goes to infinity.

The extension to "unique" geminals is discussed, but applications cannot be shown at this time due to a lack of sufficiently accurate wave functions for the range of internuclear distances that would be required.

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