Distorted *s*-type orbitals: the H_2^+ problem revisited

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On the example of the H_2^+ molecular ion, we show that spherically distorted *s*-type orbitals possessing angular dependent orbital exponents, even in a minimal basis may lead to total energies the accuracy of which is comparable with the ones obtained by fully numerical ('complete basis') calculations.

KEY WORDS: polarized s orbital, H_2^+ molecule

1.   Introduction

The principle of linear combination of atomic orbitals (LCAO) continues to serve as one of the most widespread model to construct basis functions for molecular orbital (MO) expansions in polyatomic molecules. Atomic orbitals (AOs), in most cases, are selected in the same overall form as they appear in isolated atoms: s, p, d, etc. type orbitals. Mathematically, they are chosen as irreducible representations of the rotation group that describes atomic symmetry. Merely the values of orbital exponents in the radial part of the AOs are adjusted to the molecular situation. Accordingly, the shape of a usual AO can be specified as

$$\chi(r, \vartheta, \varphi) = f(r) Y(\vartheta, \varphi),$$

where the radial part $f(r)$ is usually a linear combination of Gaussians, while $Y(\vartheta, \varphi)$ is a member of spherical harmonics describing the angular dependence according to rotational symmetry.

In a molecular environment, of course, rotational symmetry does not hold anymore, and to describe the polarization of atoms in molecules, AOs with high-azimuthal quantum numbers have to be included in the basis set. For example, while the valence orbitals in the H_2 molecule are basically constructed from *s*-type AOs centered on the two H atoms, accurate description

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of the molecule requires the inclusion of p, eventually d or higher, polarization functions. Off-centered (floating) bond-functions are sometimes used to describe the same effect, but their application is not too general due to some technical problems, e.g., the large basis set extension error they generate. In addition, using off-centered functions one gives up the LCAO principle.

In this paper, we report an idea which remains solely on LCAO grounds, but by means of it polarization effects can be described even in a minimal basis. We shall illustrate this idea on the concept of distorted s-type orbitals, and present preliminary applications on the simplest possible model, the H_2^+ molecular ion, for which analytical solutions are available.

2. Distorted s-Orbitals

In this paper, dealing with a two-center problem, we consider exponential orbitals rather than Gaussians. In the standard mathematical representation of 1s orbitals,

$$\chi_{1s}(r) = \mathcal{N}e^{-\zeta r} \tag{1}$$

(here $\mathcal{N}$ is the appropriate normalization factor), the orbital exponent, ζ, is a constant, making the 1s AO spherically symmetric. The value of this constant is ideally determined by the variational principle, making the energy of the polyatomic system stationary with respect to variations in ζ.

A simple but powerful way to describe polarization of this orbital induced by the molecular environment is to allow the exponent to depend on the polar angles ϑ, φ. (We use a spherical coordinate system where ϑ measures the angle from axis z, while φ is the angle between axis x and the xy projection.) A general form of a distorted (un-normalized) exponential 1s orbital thus reads:

$$\chi(r) = e^{-\zeta(\vartheta,\varphi)r}. \tag{2}$$

In a two-center problem, choosing the molecular axis as direction z, cylindrical symmetry eliminates the φ dependence and one is left with the less general form

$$\chi_s(r) = e^{-\zeta(\vartheta)r}. \tag{3}$$

In principle, the total energy of the two-center molecule will now be a functional of the function $\zeta(\vartheta)$, and the latter should be derived by setting the variation of this energy functional zero. The resulting Euler–Lagrange equations would be much too complicated to be soluble. Therefore, in the spirit of the Ritz method, we use the following simple variational Ansatz:

$$\zeta(\vartheta) = \zeta_0 + a\cos(\vartheta) \tag{4}$$
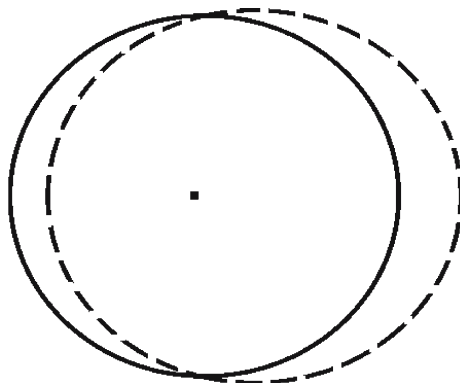
Figure 1. Schematic projection of a spherically symmetric ($\alpha = 0$) and a distorted ($\alpha = -0.6$) s-type orbital. The lines connect the points where r^2 times the orbital function has maximal values. The dimensionless parameter α is given in units of the equilibrium H_2^+ distance.

and make zero the energy derivatives with respect to the scalar parameters ζ_0 and a. So the distorted 1s orbitals are written as

$$\chi_s(r) = e^{-(\zeta_0 + a \cos(\vartheta))r} = e^{-\zeta_{0r}} e^{-a \cos(\vartheta)r}, \tag{5}$$

where, in order to ensure square-integrability of $\chi_s(r)$, we require that

$$\zeta_0 > |a| \geq 0.$$

If the positive z-axis (corresponding to direction $\vartheta = 0$) points toward the neighboring atom, a negative value for a will ensure that the exponent in the inter-atomic domain is smaller, while in the backward direction ($\vartheta = 180°$) larger than the mean exponent ζ_0, which is effectively the exponent in the perpendicular directions, $\vartheta = \pm 90°$. Since the larger (smaller) value of the exponent represents faster (slower) decay in the wave function, this simple way of making the orbital exponent angle-dependent describe the polarization of an originally symmetric s orbital toward the molecular axis. A simple illustration of such a distortion is presented in figure 1.

3. The H_2^+ Problem

We demonstrate the usefulness of distorted s orbitals on the simplest molecular system, the H_2^+ ion. This is a two-center, one-electron problem, so the evaluation of molecular integrals is feasible. The Born–Oppenheimer electronic Hamiltonian is, in atomic units

$$H = -\frac{1}{2}\Delta - \frac{1}{|r - R_A|} - \frac{1}{|r - R_B|}, \tag{6}$$

where $R_A(R_B)$ is the position vector of the hydrogen nucleus $A(B)$. Exact solution of the corresponding one-electron Schrödinger equation is possible [1, 2] in the form of an infinite, convergent series. This solution will serve us as a reference.

The simplest meaningful approximation to the (un-normalized) ground state wave function is given by the two-term (minimal basis) expansion

$$\psi(r) = \chi_{1s_A}(r) + \chi_{1s_B}(r), \tag{7}$$

where $\chi_{1s_B}(r)$ is the minimal basis 1s-type AO in form of equation (1) centered at site $X(X = A, B)$. Since the form of this expansion is determined by symmetry, the only variational parameter in equation (7) is the orbital exponent ζ. The energy expectation value as computed by this wave function,

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} + E_{\text{nuc}} \tag{8}$$

with $E_{\text{nuc}} = 1/R_{AB}$ being the nuclear repulsion energy. These values, computed at equilibrium H–H distances, are shown in the first two lines of table 1 for unoptimized (hydrogenic) and optimal exponents. As compared to the exact non-relativistic Born–Oppenheimer energy (last line in table 1), the effect of exponent optimization is quite significant but even the energy of the optimized exponential 1s orbital is only a crude approximation. Adding a polarization function (a single $2p_z$ orbital) with optimized coefficient and exponents [3] (third line in table 1) drastically improves the approximation.

The energies of the H_2^+ ion as obtained in some standard quantum chemical basis sets are collected in lines 4–7 of table 1 for comparison. It seems that basis sets of TZP quality are needed to reach mH accuracy.

Energy evaluation with the distorted s-type orbitals, equations (3) or (5), which is the aim of the present paper, requires the evaluation of new types of one-electron integrals which cannot be found in classical works [5]. To collect the necessary integrals, one substitutes $\chi_s(r)$ of (5) for χ_{1s} in equation (7), and puts the Ansatz into (8) with the Hamiltonian (6). For atom B, one takes $-\alpha$ for α, to ensure appropriate distortion orientation. The following integrals occur:

1. Normalization integral

$$n = \langle \chi_{s_A} | \chi_{s_A} \rangle.$$

2. Overlap integral

$$s = \langle \chi_{s_A} | \chi_{s_B} \rangle.$$

3. Diagonal kinetic energy integral

$$t_A = \left\langle \chi_{s_A} | -\frac{1}{2}\Delta | \chi_{s_A} \right\rangle.$$

Table 1
Total energies of the H_2^+ ion at equilibrium geometry in various basis sets and various approximations.

Basis set type	Exponents/parameters	Total energy, a.u.	References
Exponential, minimal 1s	1.0 (Hydrogenic)	−0.5654	
Exponential, minimal 1s	1.24 (Optimized)	−0.5871	
Exponential, polarized sp	Optimized	−0.6003	[3]
Gaussian, double zeta (DZ)	6-31G	−0.5840	
Gaussian, DZP	6-31G**	−0.5945	
Gaussian, triple zeta (TZ)	6-311G	−0.5905	
Gaussian, TZP	6-311G**	−0.6012	
Minimal, distorted *s*	Optimized	−0.6006	This work
James (Off-centered)	Optimized	−0.6018	[4]
Complete (Numerical solution)	–	−0.60263	[1, 2]

4. Off-diagonal kinetic energy integral

$$t_{AB} = \left\langle \chi_{s_A} \left| -\frac{1}{2}\Delta \right| \chi_{s_B} \right\rangle.$$

5. Diagonal electron attraction integral

$$u_A = -\left\langle \chi_{s_A} \left| \frac{1}{|r - R_A|} + \frac{1}{|r - R_B|} \right| \chi_{s_A} \right\rangle.$$

6. Off-diagonal electron attraction integral

$$u_{AB} = -\left\langle \chi_{s_A} \left| \frac{1}{|r - R_A|} + \frac{1}{|r - R_B|} \right| \chi_{s_B} \right\rangle$$

Evaluation of these integrals can be performed either in a spherical or in an elliptical coordinate system. The elliptical coordinates are introduced as

$$\mu = \frac{r_A + r_B}{R_{AB}},$$
$$\nu = \frac{r_A - r_B}{R_{AB}},$$

where the two-center coordinates are defined as $r_A = |r - R_A|$ and similarly for r_B. A third coordinate, φ, the angle of rotation around the molecular axis, is common in the spherical and elliptical systems. Parameters r_A, r_B, multiplied by $\cos\vartheta_A$, $\cos\vartheta_B$, respectively, as they appear in the formula (5) for the distorted s orbital, can be expressed by the elliptical coordinates using cosine theorem as

$$r_A \cos \vartheta_A = \frac{\mu\nu + 1}{2} R_{AB}, \tag{9}$$

$$r_B \cos \vartheta_B = \frac{\mu\nu - 1}{2} R_{AB}, \tag{10}$$

leading to the representation of the (unnormalized) distorted s AOs in elliptical coordinates

$$\chi_A(r) = e^{-(\rho(\mu+\nu)+\alpha(\mu\nu+1))/2} \tag{11}$$

and

$$\chi_B(r) = e^{-(\rho(\mu-\nu)-\alpha(\mu\nu-1))/2}, \tag{12}$$

where the shorthands

$$\rho = \zeta_0 R_{AB}$$

and

$$\alpha = a R_{AB}$$

are introduced as dimensionless parameters.

With this representation, the analytical result of the integrations listed above is collected as

1.

$$n = \pi R_{AB}^3 \frac{\rho}{(\rho^2 - \alpha^2)^2},$$

2.

$$s = \frac{\pi R_{AB}^3}{3} \frac{\rho^2 + 3\rho + 3}{\rho^3} e^{-(\rho+\alpha)},$$

3.

$$t_A = \frac{\pi}{2} R_{AB} \frac{\rho}{\rho^2 - \alpha^2},$$

4.

$$t_{AB} = -\frac{\pi}{2} R_{AB} e^{-(\rho+\alpha)} \left(\frac{(\rho+\alpha)^2}{3\rho} - \frac{(\rho^2-\alpha^2)(\rho+1)}{\rho^3} + \frac{2\alpha}{3\rho} \right),$$

5.

$$u_A = -2\pi R_{AB}^2 \left(\frac{1}{\rho^2 - \alpha^2} - s \right),$$

6.

$$u_{AB} = -2\pi R_{AB}^2 \frac{\rho + 1}{\rho^2} e^{-(\rho + \alpha)},$$

where S denotes the following integral

$$S = e^{-\alpha} \int_1^{\infty} \left(\frac{\cos h(\rho + \alpha\mu)}{(\rho + \alpha\mu)} - \frac{\sin h(\rho + \alpha\mu)}{(\rho + \alpha\mu)^2} \right) e^{-\rho\mu} d\mu. \tag{13}$$

Since the primitive function of this integrand cannot be found, S can be computed by expanding the hyperbolic functions into Taylor series, leading to the following fast-convergent expansion

$$S = \frac{e^{-\alpha + \rho}}{\rho} \sum_{n=1}^{\infty} \sum_{i=0}^{2n-1} \frac{(\rho + \alpha)^{2n-1-i}(\frac{\alpha}{\rho})^i}{(2n - 1 - i)!(2n + 1)}, \tag{14}$$

which is convenient to convert into the recursion formula

$$S_{k+1} = \frac{(\rho + \alpha)^{2k}}{(2k)!(2k + 3)} \left(\frac{\rho + \alpha}{2k + 1} + \frac{\rho}{\alpha} \right) + \frac{2k + 1}{2k + 3} \left(\frac{\alpha}{\rho} \right)^2 S_k, \tag{15}$$

initialized by

$$S_1 = \frac{1}{3} \left(\rho + \alpha + \frac{\alpha}{\rho} \right).$$

In our experience, this recursion converges in 5–10 steps to 10 figures accuracy.

These integrals reduce to the standard ones [5] in the $\alpha \to 0$ limit.

Once the above integrals have been evaluated, the energy expectation value is straightforward to evaluate and minimize with respect to parameters ρ and α. At equilibrium distance we obtained the values $\rho = 2.5496$ and $\alpha = -0.4710$. Since $\rho = \zeta_0 R_{AB}$, and our equilibrium distance is $R_{AB} = 2.0019$ (practically the exact result), this means that the mean exponent of the optimized distorted s AO is $\zeta_0 = 1.2736$, a value slightly larger than 1.24, the optimized exponent of the spherically symmetric exponential orbital. The effective exponent in the $\vartheta = 0$ direction (between the two nuclei) is $\zeta_0 + a = 1.0383$, which is significantly smaller than the value of the spherical exponent. In the backward direction we get $\zeta_0 - a = 1.5088$ indicating an enhanced decay of the wave function. This behavior is shown in figure 2. clearly showing the increased accumulation of electrons in the bonding region. The associated energy, as indicated in the 8th row of table 1, differs only by 2 mH from the exact numerical result. With spherical Gaussians, a contracted basis set of TZP quality should be used to achieve such an accuracy, or one should use the special James-type offcentred exponentials depending directly on elliptical coordinates [4] to get better energy.
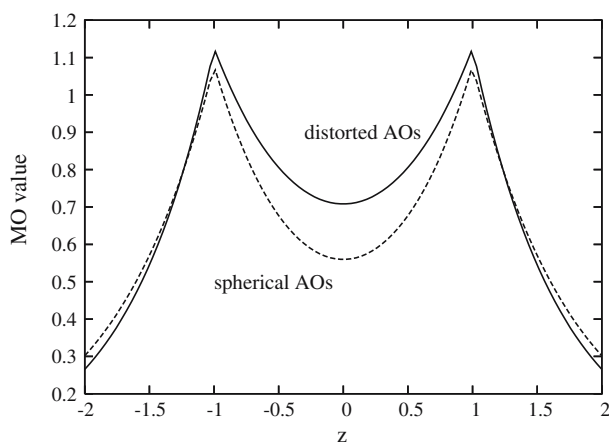
Figure 2. Value of the unnormalized bonding MO in the $x = y = 0$ cross-section as a function of z, composed from optimal spherical (dashed line) and distorted (solid line) 1s orbitals.
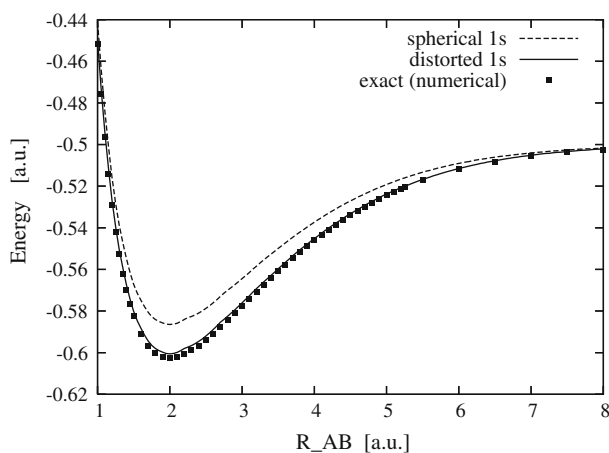

Figure 3. Potential curve of H_2^+ obtained by the minimal basis set of spherically symmetric 1s AOs and with distorted s orbitals as compared to the exact non-relativistic Born–Oppenheimer curve. The latter is taken from the data in Ref. 2.

Apart from equilibrium results, it appears to be interesting to have a look on the potential curve of H_2^+. In figure 3, we plotted the curves computed by spherically symmetric and distorted orbitals, as well as the exact numerical curve taken from Ref. 2. The improvement obtained by distortion is well seen: the optimized result, although it corresponds to a minimal basis, can hardly be distinguished from the exact curve on this scale.
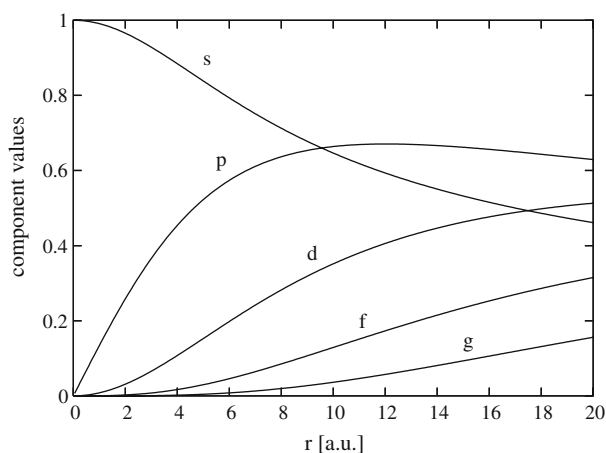
Figure 4. r-dependence of the expansion coefficients C_l of equation (16) for $l = 0, 1, 2, 3$, and 4 (s, p, d,..., respectively) for $0 < r \leq 20$ a.u.

4. Expansion in terms of spherical harmonics

Distorted s-orbitals can be related to traditional functions by considering the expansion of their angular part

$$e^{-\zeta(\vartheta)r} = \sum_{l}^{\infty} C_l(r) Y_{lo}(\vartheta) \qquad (16)$$

in terms of spherical harmonics with $m = 0$. The expansion coefficients, C_l, remain dependent on the radial coordinate. Such an expansion is readily carried out due to the orthogonality of spherical harmonics. The result is plotted in figure 4. showing that for small r the distorted orbital is dominated by its $l = 0$ component, i.e., the spherical s orbital. As the distance from the nucleus increases, the p component ($l = 1$) starts growing, and at around $r = 9$ it starts to have the largest weight. For higher l values the effect is similar: they have a negligible contribution around the origin, but their role starts to increase slowly with growing r. For even larger r values, the curves exhibit a maximum for $l \geq 1$, while the s component decreases monotonically. The maximum of the p component is seen at around 11 a.u., while the plots for larger l have their maxima outside of the range of figure 4.

5. Outlook and conclusion

This work reported an idea of using orbital exponents of s-type functions, which depend on azimuthal directions leading to orbitals capable of describing polarization effects. The magnitude of the angle dependence has been optimized

variationally. The resulting orbitals are termed as distorted s orbitals. The idea was tested on the simplest example of the H_2^+ molecular ion for which a great improvement in the accuracy of energies has been resulted.

Generalization of this idea to many-electron and multi-center systems is possible, but not easy. As soon as one deals with two or more electrons, the problem of evaluating two-electron repulsion integrals has to be solved, which appears to be much more difficult than that of the one-electron integrals we have dealt with above. The situation is even more complicated in polyatomic molecules, since there not only integral evaluation seems to be cumbersome, but also the guessing of the functional form of the distortion (cf. equation (4)) requires more intuition. Nevertheless, it is a challenging project to see whether the accuracy improvement reported here for H_2^+ can also be found in these more complicated cases. Work in these lines is in progress.

Acknowledgment

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