An Application to H_2^+ of Laplace Type Integral Transform and its Inverse

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Laplace type integral transformation (LIT) has been applied to wavefunctions. The effect of the inverse transform is also discussed. LIT wavefunctions are tested in the calculation of the ground-state energy of H_2^+, where the untransformed functions were 1s, 12s, 123s and 1234s-STO. The results presented here show that LIT wavefunctions are applicable in molecular computations. The analytical formulae for two-centre one-electron integrals over LIT wavefunctions are derived by use of a Barnett-Coulson-like expansion of $r_b^N (r_b + p)^{-\nu}$.

I. Introduction

The hydrogen molecule ion H_2^+ has already been studied in 1922 by Pauli [1] who had used Bohr quantum theory. The separation of the variables entering the problem was made possible by use of confocal elliptical coordinates. The Schrödinger equation becomes separable as well by use of these coordinates as it was shown in 1927 by Burrau [2]. Among many papers on the same subject the results of Bates, Ledsham and Stewart [3] are distinguished by their accuracy and serve for the comparison with approximate results on H_2^+.

An approximate integral transformation wavefunction was introduced into nuclear physics by Wheeler [4] and Griffin and Wheeler [5]. It has the following form

$$\Psi(\boldsymbol{x}) = \mathcal{L}\Phi = \int \Phi\,(\boldsymbol{x}, \alpha)\, f(\alpha)\, \mathrm{d}\alpha\,, \tag{1}$$

where $\boldsymbol{x}$ denotes the position of a particle and α stands for the generator coordinate. $f(\alpha)$ is the generator function, and in Refs. [4] and [5] it has been determined by means of the variational principle. The wavefunction before transformation is denoted by Φ.

Integral transformation wave functions have also been introduced into molecular structure computations. The first attempt was done by Somorjai [6] and later by many other authors [7 – 22]. Different generator functions and orbitals have been assumed and applied in computations of simple molecular systems. The expectation value of the energy E, for a given integral transformation wavefunction, $\Psi = \mathcal{L}\Phi$, is given by

$$\langle \mathcal{L}\Phi \,|\, H \,|\, \mathcal{L}\Phi \rangle = E \langle \mathcal{L}\Phi \,|\, \mathcal{L}\Phi \rangle\,, \tag{2}$$

where H denotes the Hamiltonian of the molecule under consideration.

On the other hand, the integral transformation, $\mathcal{L}$, could be applied to the matrix element of the Hamiltonian and the overlap integral, which was done by Jakab and Randić [20] and results in the expression

$$\mathcal{L}[\langle \Phi \,|\, H \,|\, \Phi \rangle] = \mathcal{L}[E(\alpha) \langle \Phi \,|\, \Phi \rangle]\,. \tag{3}$$

Some criticism should be given to this method:

The energy of the untransformed function $\Phi \equiv \Phi(\boldsymbol{x}, \alpha)$ depends on the generator coordinate α and is given by

$$\langle \Phi \,|\, H \,|\, \Phi \rangle = E(\alpha) \langle \Phi \,|\, \Phi \rangle\,. \tag{4}$$

After the integral transformation $\mathcal{L}$ has been applied one obtains (3), where integration is done over the generator coordinate α. The ratio $\mathcal{E}$ between the lhs. of (3) and $\mathcal{L}\langle \Phi \,|\, \Phi \rangle$

$$\mathcal{E} = \frac{\mathcal{L}\langle \Phi \,|\, H \,|\, \Phi \rangle}{\mathcal{L}\langle \Phi \,|\, \Phi \rangle} \tag{5}$$

is by no means the energy of $\mathcal{L}\Phi$ as it was assumed in [20]. The energy obtained by Jakab and Randić is in fact close to the energy of the untransformed

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function Φ because the variation of the parameters they considered corresponds to the application of the inverse transform $\mathscr{L}^{-1}$. The interplay between the choice of parameters and the application of $\mathscr{L}^{-1}$ will be treated in the next section.

The aim of the present paper is the application of trial wavefunctions which are obtained by use of the Laplace type integral transformation (LIT) according to (2). The analytical expressions for two-centre one-electron integrals over transformed functions are derived. The energy of the ground state of H_2^+ is calculated and a substantial improvement is achieved in comparison with the cases where untransformed functions are considered. Until now such an improvement for LIT wavefunctions was realized only for atomic systems [22] but never for molecular systems, which has discouraged wider use of LIT wavefunctions. The wavefunction used in the present paper is a linear combination of the LIT functions.

It is also shown under which conditions the transformed function reduces to the untransformed function.

II. Laplace Type Integral Transformation Wavefunction

In the following text Laplace type integral transformation $\mathscr{L}$, with the weighting function

$$f(\alpha, q, p) = [\Gamma(q p)]^{-1} p^{qp} \alpha^{qp-1} e^{-\alpha p}, \qquad (6)$$

will be considered, where q and p are positive parameters. The integration over the generator variable α in definition (1) runs from zero to infinity.

As an untransformed function a very general function

$$\Phi = F(\boldsymbol{r}, S)\, \alpha^n \exp[-\alpha g(r, Q)] \qquad (7)$$

has been chosen. Here $\boldsymbol{r}$ denotes the position vector and S and Q represent some sets of parameters. The functions F and g are not dependent on the parameter α.

By the use of (2) and (3) the energy E and the quantity $\mathscr{E}$, respectively, can be calculated for the $\mathscr{L}$ introduced above. It can be shown, having in mind the definition of $e^z = \lim_{p \to \infty} (1 + z/p)^p$, that $\mathscr{L}^{-1}(\,)$ can be replaced by $\lim(\,)$. This enables us to return easily to the original number of transform. However, in the numerical applications it is sufficient to take p as an sufficiently large number. Then q and other parameters are optimized as usually. The convergency toward e^z is very slow. The quantity $|e^z - (1 + z/p)^p|$ is of the order of $(1/p)$.

III. Evaluation of Two-Centre One-Electron Integrals

For the untransformed atomic orbital (7) $(N + 1)$s-STO orbital, $\Phi(N, \alpha, r_a) = r_a^N \exp(-\alpha r_a)$ is chosen. Index a refers to the atomic nucleus. The weighting function is defined by (6). A simple derivation leads to the following expression for the atomic integral transformation wavefunction:

$$\chi = (2\pi)^{-1/2} r_a^N (1 + r_a/p)^{-n}, \qquad (8)$$

where n is a positive number and $n > (N + 3)$. In the special case when $p \to \infty$, $n = qp \to \infty$ and $q \to \alpha$, χ becomes the original orbital Φ. Accordingly, in the evaluation of the energy of a molecule the calculation of the following two-centre one-electron integral is needed:

$$\begin{aligned} A &\equiv A(n, m, k, p, R, N, N') \qquad (9)\\ &= (2\pi)^{-1} \int r_a^{N-k} (1 + r_a/p)^{-n} (1 + r_b/p)^{-m} r_b^{N'} \, d\tau, \end{aligned}$$

where a and b refer to atomic nuclei, $n = q p$ and $m = q' p$ are defined by the weighting function for Φ_a and Φ_b, k is zero or one, and R denotes the internuclear distance.

The integral (9) could be evaluated in many different ways. The first possibility is offered by use of confocal ellipsoidal coordinates, but difficulties appear because of a singularity for $r_a = r_b$. The second approach is based on the use of bipolar coordinates [23]. The third approach is based on the expansion of the function located at b about another centre a. The starting point is the Barnett-Coulson expansion [24] of $(N + 1)$s-STO which is given by

$$\begin{aligned} r_b^N \exp(-\alpha r_b) &= (2\pi)^{1/2} \sum_{L=0}^{\infty} \qquad (10)\\ &\cdot (r_a R)^{-1} B_{L, N+1}(r_a, R, \alpha)\, Y_{L0}(\Omega_a), \end{aligned}$$

where Y_{L0} are the spherical harmonics. The B functions are defined in [23] as

$$\begin{aligned} &B_{L,N}(r_a, R, \alpha) \qquad (11)\\ &= \int_{|R-r_a|}^{R+r_a} r_b^N \exp(-\alpha r_b)\, \Theta_{L,0}(\cos \vartheta_a)\, dr_b, \end{aligned}$$

where the normalized Legendre functions have the form [25]

$$\Theta_{L,0}(\cos\vartheta_a) = 2^{-L}((2L+1)/2)^{1/2} \cdot \sum_{i=0}^{L} \binom{L}{i}^2 (\cos\vartheta_a - 1)^i (\cos\vartheta_a + 1)^{L-i}. \tag{12}$$

Having in mind that $\cos\vartheta_a = (r_a^2 + R^2 - r_b^2)/(2Rr_a)$, the B functions are not angularly dependent.

The application of LIT to (10) under the assumption that $m > -1$ and $p > 0$ yields

$$r_b^N (1 + r_b/p)^{-m} = (2\pi)^{1/2} \cdot \sum_{L=0}^{\infty} (r_a R)^{-1} B^T_{L,N+1}(r_a, R, m, p)\, Y_{L0}(\Omega_a), \tag{13}$$

where the B^T-functions are given by

$$B^T_{L,N}(r_a, R, m, p) = \int_{|R-r_a|}^{R+r_a} r_b^N (1 + r_b/p)^{-m} \cdot \Theta_{L,0}(\cos\vartheta_a)\, \mathrm{d}r_b. \tag{14}$$

By taking expansion (13) into account, the two-center one-electron integrals (9) could be written as

$$A = R^{-1} \int_0^{\infty} \mathrm{d}r_a\, r_a^{N+1-k} (1 + r_a/p)^{-n} \cdot \int_{|R-r_a|}^{R+r_a} r_b^{N'+1} (1 + r_b/p)^{-m}\, \mathrm{d}r_b. \tag{15}$$

Note that the introduction of bipolar coordinates in (9) yields the same result.

Further, (15) is broken into three parts:

$$A = p^{N1+N'+3}/R \sum_{i=0}^{N'+1} \binom{N'+1}{i} (-1)^{N'-i} \cdot M^{-1} \left[\int_0^{\infty} t^{N1} (1+t)^{-n} (1+G+t)^{-M}\, \mathrm{d}t - \int_0^{G} t^{N1} (1+t)^{-n} (1+G-t)^{-M}\, \mathrm{d}t - \int_G^{\infty} t^{N1} (1+t)^{-n} (1-G+t)^{-M}\, \mathrm{d}t \right], \tag{16}$$

where $N1 = N + 1 - k$, $M = m - i - 1$ and $G = R/p$. If n and m are integers, the integrals which appear in (16) could be expressed as finite sums. These sums are alternating ones, and in the case of large n rounding errors occur. By having this in mind as well as by removing the assumption that n and m are integers, the integrals in (16) are rather expressed as infinite converging binomial series. Consequently, the following three types of integrals in (16) appear if $p > R$:

$$B \equiv B(N1, n, M, G) = \int_0^{\infty} t^{N1} (1+t)^{-n} (1+G+t)^{-M}\, \mathrm{d}t = \sum_{j=0}^{N1} \binom{N1}{j} (-1)^{N1-j} \sum_{l=0}^{\infty} \binom{M+l-l}{l}' \cdot (-G)^l/(n+M+l-j-1), \tag{17}$$

$$\begin{aligned} D \equiv D(N1, n, M, G) &= \int_0^{G} t^{N1} (1+t)^{-n} (1+G-t)^{-M}\, \mathrm{d}t \\ &= (2+G)^{-M} \sum_{j=0}^{N1} \binom{N1}{j} (-1)^{N1-j} \left\{ \sum_{\substack{l=0 \\ l \neq n-j-1}}^{\infty} \binom{M+l-1}{l}' (2+G)^{-l} (n-j-l-1)^{-1} \right. \\ &= \left. [1 - (1+G)^{j-n+l+1}] + (2+G)^{j-n+1} \binom{M+n-j-2}{n-j-1}' \ln(1+G) \right\}, \end{aligned} \tag{18}$$

$$\begin{aligned} C \equiv C(N1, n, M, G) &= \int_G^{\infty} t^{N1} (1+t)^{-n} (1-G+t)^{-M}\, \mathrm{d}t \\ &= \sum_{j=0}^{N1} \binom{N1}{j} (-1)^{N1-j} \sum_{l=0}^{\infty} \binom{M+l-1}{l}' G^l (1+G)^{j-n-M-l+1}/(n+M+l-j-1), \end{aligned} \tag{19}$$

$$BC = B - C = -2 \sum_{j=0}^{N1} \binom{N1}{j} (-1)^{N1-j} \sum_{l=0}^{\infty} \binom{M+l-l}{l}' G^l [(-1)^l - (1+G)^{-n-M-1+j+1}]/(n+M+l-j-1). \tag{20}$$

Table 1. The total ground state energy E (in a.u.) of the hydrogen molecule ion H_2^+ for the equilibrium internuclear distance $R = 2.$ a.u. with 1s-LIT function.

qp	3	20	50	100	500	1000	5000	10 000
p	1.310	14.87	39.09	79.44	402.4	806.1	4036.0	8073.0
$-E$	0.4399	0.5600	0.5843	0.5855	0.5863	0.5864	0.5865	0.5865

$-E_{\text{exact}} = 0.6026$ Ref. [3]

Table 2. Comparison of the energy for the state of H_2^+ at $R = 2.$ a.u. with different variational functions.

Atomic orbitals on each nucleus	Energy a.u.	References
1s-STO	−0.5865060	This work
12s-STO	−0.590450	Bishop and Schneider [9]
1234s-STO	−0.590502	Bishop and Schneider [9]
123s-LIT	−0.5908398	This work
1234s-LIT	−0.5908432	This work
Two-centre spherical limit	−0.590891	Schwartz and Schaad [27] and Katriel and Adam [28]

If $p < R$, analogous expressions could be derived. $\binom{n}{r}'$ is a binomial coefficient for n being an integer while for n being not an integer it is given by $n(n-1)\ldots(n-r+1)/r!$ and in addition $\binom{n}{0}' = 1$.

Finally, the two-centre integrals (9) for $p > R$ are given:

$$A = p^{N+N'+4-k}/R \qquad (21)$$

$$\cdot \sum_{i=0}^{N'+1} \binom{N'+1}{i} (-1)^{N'-i}(BC-D)/(m-i-1)\,.$$

IV. The ground-state energy of H_2^+

For the untransformed wavefunction describing the ground-state of H_2^+ a linear combination of m s-type STO orbitals, $\Phi(\alpha, r) = \exp(-\alpha r) \sum_{i=0}^{m} C_i r^i$ placed on each centre, is chosen. The application of the integral transformation considered here yields the following transformed wavefunction:

$$\Psi_a = (2\pi)^{-1/2}(1 + r_a/p)^{-qp} \sum_{i=0}^{m} C_i r_a^i\,. \qquad (22)$$

The total energy E for the one 1s-LIT wavefunction on each nucleus has been calculated for a series of values of qp. For the given qp the parameter p has been optimized. Some results for the equilibrium distance of nuclei, $R = 2\,au$, are presented in Table 1. The table shows that the order of the magnitude of qp determines the number of significant figures of E. This is further illustrated by the following data: $E = -0.58649640$, -0.58650502 and $-0.58650598\,au$ for $qp = 10^4$, 10^5 and 10^8, respectively. Note that the minimum of energy is not achieved before $qp \to \infty$. This means that our results with the 1s-Laplace integral transform wavefunction reproduce the results obtained with inverse, untransformed linear combination of 1s-STO [26] in which case $E = 0.586506\,au$, Bishop and Schneider [9].

Furthermore, the linear combinations of 1s2s, 1s2s3s and 1s2s3s4s-LIT functions on each centre with common q and p were fully optimized together with their linear coefficients.

We have found that on minimizing the energy with respect to the variational parameters q and p, the linear combinations 1s2s-LIT wavefunctions reduce to their untransformed functions, i.e. to the linear combinations 1s2s-STOs ($p \to \infty$). For example, we have found out the energy value $E = -0.590449\,au$ for the parameters $qp = 10^5$ and $p = 6.142072\;10^4$. It is obvious that from these values the inverse transformation appeared: 1s2s-STO [9] (Table 2).

For the linear combinations 1s2s3s-LIT wavefunctions the minimum is obtained for the parameters $qp = 101.513$, $p = 48.5307$, and the energy was $E = -0.5908398\,au$, which is better than the energy of untransformed linear combinations 1s2s3s4s-STOs $-0.590502\,au$ [9]. Since this is close to the spherical limit [27, 28] for the H_2^+ ion, the result obtained for $qp = 109.723$ and $p = 47.9028$ of the 1s2s3s4s-LIT wavefunctions was only slightly lower: $E = -0.5908432\,au$.

In spite of the fact that we minimized only two nonlinear parameters in all cases we are not quite sure that a real minimum is obtained because of the existence of more minima for the given functions.

By the grid search method the region of a sharp and steep minimum for 1s2s3s-LIT wavefunctions was found which by standard optimization methods had not been found.

By this paper it has been shown that the linear combinations of the 1s2s3s-LIT wavefunctions and 1s2s3s4s-LIT wavefunctions give considerably better energy values than the linear combinations of the 1s2s3s4s-STOs for H_2^+ ion. This advocates their application in molecular calkculations. For this reason s-type two-centre one-electron integrals, here developed, could be useful.

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