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On the implicit integral character of Roothaan's expansion

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Abstract. The molecular generator coordinate Hartree-Fock method is reviewed. The connection between a quadrature solution of the generator coordinate Hartree-Fock equations and Roothaan's equations is stressed. The relation between linear expansion coefficients and generator coordinate weight functions is discussed and a numerical and analytical example is provided for the 1s orbital of the hydrogen atom represented as the integral transform of a Gaussian function. For the same example, the Gauss-Labatto quadrature is employed to emphasize the implicit integral character of Roothaan's equations. As a major conclusion, the interpretation that every LCAO calculation is actually performing integrations of the Griffin-Wheeler equations is advanced. Basis sets are therefore abscissas of the implicit quadrature used in the integration, whereas the linear coefficients automatically incorporate the corresponding weights. Subsequently, it is shown how to extract the generator coordinate weight function from the LCAO coefficients which has the advantage of being a characteristic of the physical system under study and not of the particular calculation being carried out. As such, basis set design becomes how to efficiently sample the weight function.

PACS. 31.15.Ar Ab initio calculations

1 Introduction

The variational generator coordinate method was introduced by Griffin and Wheeler [1] in 1957 and has proven to be useful in the solution of one particle problems. In this formulation the trial one particle function is given by the integral transform

$$\psi(x) = \int F(\zeta)\varphi(x,\zeta)d\zeta, \tag{1}$$

where $\varphi(x,\zeta)$ is the generator function, $F(\zeta)$ is a weight function, x denotes space and spin variables, and ζ is the generator coordinate – the integration being carried out through the whole domain of $\varphi(x,\zeta)$ in ζ. As such, the generator function is a functional form only, whereas $F(\zeta)$, the weight function, is allowed to vary until a minimum value of the energy is obtained.

In 1986, the generator coordinate *ansatz* was applied to the Hartree-Fock theory of atoms [2]. Various applications to atomic systems followed aiming at the design of universal atomic basis sets [3].

In 1991, DaCosta *et al.* [4] presented the molecular Generator Coordinate Hartree-Fock method for closed shell systems. The key to this method is the functional form of the molecular orbital for electron ν of a system of 2I electrons and N nuclei be written as

$$\psi_i(\nu) = \sum_{n=1}^{N}\int F_{i,n}(\zeta)\varphi(\zeta,\mathbf{r}_\nu-\mathbf{R}_n)d\zeta. \tag{2}$$

By taking the trial function Ψ as a Slater determinant over the ψ_i, the expression for the electronic energy is

$$E = 2\sum_{i}^{I} h_{ii} + \sum_{i}^{I}\sum_{j}^{I}(2J_{ij}-K_{ij}), \tag{3}$$

where, as usual, h, J, and K have their usual meaning.

Variation of E with respect to the $F_{i,n}(\zeta)$ keeping $\psi_i(\nu)$ normalized leads to the molecular Griffin-Wheeler-Hartree-Fock (GWHF) equations

$$\sum_{n=1}^{N}\int d\zeta[F_{n,n'}(\zeta,\zeta')-\epsilon_i S_{n,n'}(\zeta,\zeta')]F_{i,n}(\zeta) = 0, \qquad i=1,\ldots,I, \tag{4}$$

where the ϵ_i are the orbital energies,

$$F_{n,n'}(\zeta,\zeta') = \langle\varphi(\zeta,\mathbf{r}_\nu-\mathbf{R}_n)|h(\nu) + \sum_{j}^{I}[2J_j(\nu)-k_j(\nu)]|\varphi(\zeta',\mathbf{r}_\nu-\mathbf{R}_{n'})\rangle \tag{5}$$

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and

$$S_{n,n'}(\zeta,\zeta') = \langle \varphi(\zeta, \mathbf{r}_\nu - \mathbf{R}_n) | \varphi(\zeta', \mathbf{r}_\nu - \mathbf{R}_{n'}) \rangle. \quad (6)$$

The form of $\psi_i(\nu)$ in equation (2) implies that in each molecular calculation one has to determine the weight function $F_{i,n}(\zeta)$ for each orbital at each nucleus.

In this paper we discuss the relationship between the Generator Coordinate Hartree-Fock method and the LCAO (linear combination of atomic orbitals) approximation to the Hartree-Fock equations. We then recognize the importance in obtaining the weight functions, and further we show how to extract the weight functions from LCAO calculations. Finally, we replace basis set exponents by a quadrature and show that this procedure leads to the exact weight function.

2 Comparison between the generator coordinate and Roothaan's expansions and extraction of weight functions from LCAO coefficients

Replacing the integral in equation (4) by a quadrature T, with abscissae ζ_t and weights w_t, one obtains

$$\sum_n^N \sum_t [F_{n,n'}(\zeta_t,\zeta_t') - \epsilon_i S_{n,n'}(\zeta_t,\zeta_t')] w_t F_{i,n}(\zeta_t) \cong 0, \quad (7)$$

in which case the $\psi_i(\nu, T)$ approximations to $\psi_i(\nu)$, which are now parametrically dependent on the quadrature T, become

$$\psi_i(\nu) \cong \psi_i(\nu, T) = \sum_n^N \sum_t w_t F_{i,n}(\zeta_t) \varphi(\zeta_t, \mathbf{r}_\nu - \mathbf{R}_n). \quad (8)$$

Comparing equations (7, 8) with Roothaan's equation [5] one easily recognizes that the exponents of the basis set are precisely the set of abscissae of the chosen quadrature and the LCAO orbital is

$$\begin{aligned}\psi_i(\nu, T) &= \psi_i^{(LCAO)}(\nu) \\ &= \sum_n^N \sum_t C_{i,n,t} \varphi(\zeta, \mathbf{r}_\nu - \mathbf{R}_n),\end{aligned} \quad (9)$$

where

$$C_{i,n,t} = w_t F_{i,n}(\zeta_t) \quad (10)$$

are precisely the LCAO coefficients.

Roothaan's equations can therefore be understood as the discretized form of the Generator Coordinate Hartree-Fock equations. The linear coefficients can consequently be regarded as functionally dependent on ζ_t and parametrically dependent on the quadrature as a whole.

Therefore, if the purpose is to determine $F_{i,n}(\zeta)$ from a LCAO calculation [3], then, basis sets could be comprised of orbitals with exponents equal to $\zeta_t = \zeta_{min} + \delta t$, where t is the quadrature index and δ a constant [3]. For the case of Gaussian or Slater type functions a relabeling of the coordinate to Ω such that

$$\Omega = \frac{\ln \zeta}{A} \quad \text{or} \quad \zeta = e^{A\Omega} \quad (A > 1), \quad (11)$$

introduced by Mohallem [6], is very efficient for running usual calculations. Even-tempered orbitals [7], for example, have exponents equally spaced in Ω and form a highly efficient and cost-effective set of orbitals [8]. Accordingly, the form of the molecular orbitals, equation (2), becomes

$$\psi_i(\nu) = \sum_{n=1}^N \int_{-\infty}^{\infty} F_{i,n}(e^{A\Omega}) A e^{A\Omega} \varphi(e^{A\Omega}, \mathbf{r}_\nu - \mathbf{R}_n) d\Omega, \quad (12)$$

since $d\zeta = Ae^{A\Omega} d\Omega$.

Replacing the integral in equation (12) by a quadrature we obtain

$$\begin{aligned}\psi_i(\nu) &\cong \psi_i(\nu, T) \\ &= \sum_{n=1}^N \sum_t w_t F_{i,n}(e^{A\Omega_t}) A e^{A\Omega_t} \\ &\quad \times \varphi(e^{A\Omega_t}, \mathbf{r}_\nu - \mathbf{R}_n).\end{aligned} \quad (13)$$

By setting $\Delta\Omega$ constant we force the non-end point weights to be constant. For a sufficiently large number of abscissae the quadrature becomes essentially trapezoidal and, as such, equation (12) can be rewritten as

$$\begin{aligned}\psi_i(\nu, T) = \sum_{n=1}^N \sum_t \mu_t \Delta\Omega F_{i,n}(e^{A\Omega_t}) A e^{A\Omega_t} \\ \times \varphi(e^{A\Omega_t}, \mathbf{r}_\nu - \mathbf{R}_n)\end{aligned} \quad (14)$$

where $\mu_t = w_t/\Delta\Omega$ and will be found to be very close to unity for the non-end points.

The LCAO linear coefficients given by equation (10) now become

$$C_{i,n,t} = \mu_t \Delta\Omega A e^{A\Omega_t} F_{i,n}(\zeta_t), \quad (15)$$

and the weight function at abscissa ζ_t is

$$F_{i,n}(\zeta_t) = \frac{C_{i,n,t}}{\mu_t \Delta\Omega A e^{A\Omega_t}} \cdot \quad (16)$$

3 The importance of intrisinc weight functions: The ground state orbital of the hydrogen atom as an example

Given a generator function $\varphi(\zeta, \mathbf{r}_\nu - \mathbf{R}_n)$, which can be a Gaussian-type orbital (GTO), a Slater-type orbital (STO) or any other type of function, the variational task is to find the weight function $F_{i,n}(\zeta)$ which minimizes the total energy of the system under study.

The LCAO method is a way of sampling the ζ space with an adequate mesh to obtain the best energy and total wave function for the system. Here it is important to emphasize that once an arbitrary set of abscissae is taken, the LCAO procedure will automatically find weights that do not intend to minimize the error in evaluating the wave function, equation (2), but minimize the error in the simultaneous evaluation of the I integrals in equation (4) subject to the orthonormality restriction of the set of molecular orbitals.

For a given problem, once the generator function (whose integral transform can generate any function) is chosen, then the weight functions for each molecular orbital for each nucleus both exist and are unique [9]. As a result, the quest is to obtain estimates of these basis set weight functions, from which efficient atom adapted or universal basis sets can be designed.

From equation (10), the LCAO coefficients $C_{i,n,t}$ are not always measures of the weight function $F_{i,n}(\zeta_t)$. For the same molecular system in the same geometry and electronic state, a coefficient $C_{i,n,t}$ corresponding to ζ_t in one basis set can be different from another one for the same ζ_t; and thus, the weights are different despite the fact that $F_{i,n}(\zeta_t)$ is the same for both.

Likewise, plots of LCAO coefficients as functions of ζ are not plots of the weight functions $F_{i,n}(\zeta)$ because the corresponding weights w_t are not necessarily all identical.

The example that will be used in this paper will be that of the orbital of the ground state of one-electron atoms computed from GTOs. The exact radial solution of this problem is known ($\lambda = 1$ for the hydrogen atom). Written in terms of the generator coordinate *ansatz* we have

$$2\lambda^{3/2}e^{-\lambda r} = \int_0^\infty F(\lambda,\zeta)G(r,\zeta)d\zeta, \tag{17}$$

where we choose a normalized 1s GTO as generator function

$$G(r,\zeta) = \left(\frac{2\zeta}{\pi}\right)^{1/4} 2(2\zeta)^{1/2}e^{-\zeta r^2}, \tag{18}$$

and the weight function for the ground state of the one-electron atom is

$$F(\lambda,\zeta) = \left(\frac{\lambda}{2\zeta}\right)^2 \left(\frac{2\lambda^2}{\pi\zeta}\right)^{1/4} \exp\left(\frac{-\lambda^2}{4\zeta}\right). \tag{19}$$

In order to extract the weight function, one has to have an idea of the weight function because a reasonable starting value for $\Delta\Omega$, Ω_{min} must be set. Generally, an initial rough LCAO calculation should provide that. The Ω_{min} is therefore the most diffuse of the orbitals after which the others are found, *i.e.*, $\Omega_t = \Omega_{min} + t\Delta\Omega$.

By choosing $\Omega_{min} = -0.68$ ($\zeta = 0.017$) and $A = 6.0$, we performed several calculations with 17 different GTOs for the hydrogen atom case. Here it is interesting to point out that $A = 6.0$ is a optimum value for A according to the suggestion of Mohallem and Trsic [10], and it has no deep meaning in our calculations.

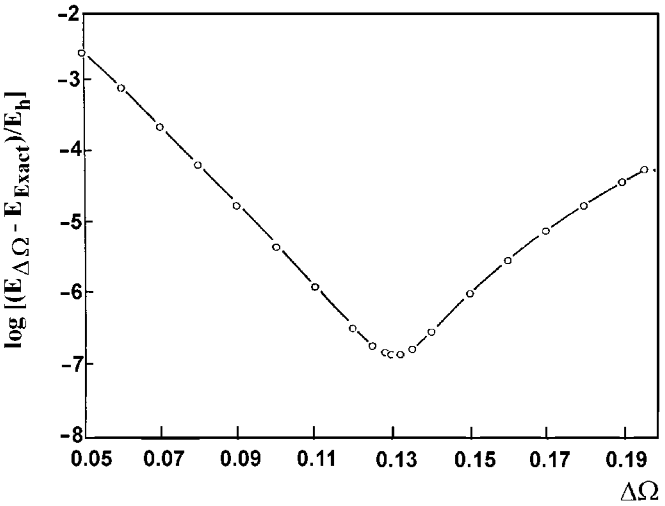

Fig. 1. Hydrogen atom ground state case: quality of the energy $\log(E_{\Delta\Omega} - E_{exact})/E_h$ as a function of $\Delta\Omega$ for 17 GTO calculations. $E_{\Delta\Omega}$ is the energy obtained in calculations for each $\Delta\Omega$, and E_{exact} is the exact energy $-0.5E_h$.

Figure 1 shows a plot of a measure of the quality of the energy, $\log[(E_{\Delta\Omega} - E_{exact})/E_h]$ (where $E_{\Delta\Omega}$ is the energy obtained for each $\Delta\Omega$ and E_{exact} is the exact energy for this problem: $-0.5E_h$), as a function of $\Delta\Omega$. Clearly, the best $\Delta\Omega$ is 0.13, and thus $\Delta\Omega = 0.13$ or larger can be used to extract the weight function.

In fact, in carrying on a LCAO calculation one is solving a numerical eigenvalue-eigenvector problem and, therefore, as the exponents become closer, the linear coefficients start to oscillate in sign besides becoming erratic in order to annihilate each other and consequently remove the quasi-linear dependency. When that happens, the quality of the resulting wave function deteriorates, and that is the reason why the energy worsens in Figure 1 for $\Delta\Omega$ lower than 0.13.

The same behavior can be seen in Figure 2 which shows plots of the LCAO coefficients as functions of Ω. The first two curves, with $\Delta\Omega = 0.18$ and 0.13 behave correctly. The third curve, with $\Delta\Omega = 0.08$, displays the above mentioned oscillations and is totally useless for the purpose of extracting the weight function.

The problem we now face is that we need to know the exact weight function which is a continuous function of ζ. On the other hand, we cannot run a LCAO calculation with an arbitrary fine mesh because of the problem discussed above. Then, how to extract the weight function inside the intervals of Ω of a given calculation? The solution we present here is to run different calculations with the same $\Delta\Omega$ and basis set size but with the Ω_{min} of the second calculation in between the first two Ω values (*i.e.*, between Ω_{min} and $\Omega_{min} + \Delta\Omega$) of the first calculation. Table 1 shows the results of two calculations performed in this manner. Clearly, the end points in each run are predictably useless. For large values of Ω (more compact GTOs) the last two LCAO coefficients don't yield good estimates of the exact weight function. For small values of Ω (more diffuse GTOs) only the first LCAO coefficient

Table 1. Comparison between the LCAO expansion coefficients C and the extracted and exact weight function F for the H-atom ground state represented by a Gaussian generator function.

Ω (generator coordinate)	C (first run)	C (second run)	$F_{extracted}$	F_{exact}
-0.680	3.73×10^{-4}		2.45×10^{-2}	8.21×10^{-4}
-0.605		-7.86×10^{-4}	-3.29×10^{-2}	6.33×10^{-2}
-0.530	2.73×10^{-2}		7.31×10^{-1}	7.01×10^{-1}
-0.455		1.36×10^{-1}	2.31	2.25
-0.380	2.99×10^{-1}		3.25	3.28
-0.305		4.15×10^{-1}	2.87	2.89
-0.230	4.20×10^{-1}		1.85	1.84
-0.155		3.42×10^{-1}	9.63×10^{-1}	9.60×10^{-1}
-0.080	2.44×10^{-1}		4.37×10^{-1}	4.39×10^{-1}
-0.005		1.61×10^{-1}	1.84×10^{-1}	1.85×10^{-1}
0.070	1.01×10^{-1}		7.39×10^{-2}	7.36×10^{-2}
0.145		6.11×10^{-2}	2.85×10^{-2}	2.84×10^{-2}
0.220	3.59×10^{-2}		1.07×10^{-2}	1.07×10^{-2}
0.295		2.10×10^{-2}	3.98×10^{-3}	3.99×10^{-3}
0.370	1.23×10^{-2}		1.48×10^{-3}	1.47×10^{-3}
0.445		7.03×10^{-3}	5.41×10^{-4}	5.40×10^{-4}
0.520	4.00×10^{-3}		1.96×10^{-4}	1.97×10^{-4}
0.595		2.30×10^{-3}	7.18×10^{-5}	7.20×10^{-5}
0.670	1.32×10^{-3}		2.64×10^{-5}	2.62×10^{-5}
0.745		7.52×10^{-4}	9.57×10^{-6}	9.54×10^{-6}
0.820	4.25×10^{-4}		3.45×10^{-6}	3.47×10^{-6}
0.895		2.44×10^{-4}	1.26×10^{-6}	1.26×10^{-6}
0.970	1.40×10^{-4}		4.60×10^{-7}	4.59×10^{-7}
1.045		7.92×10^{-5}	1.67×10^{-7}	1.67×10^{-7}
1.120	4.55×10^{-5}		6.10×10^{-8}	6.06×10^{-8}
1.195		2.61×10^{-5}	2.23×10^{-8}	2.20×10^{-8}
1.270	1.40×10^{-5}		7.65×10^{-9}	7.80×10^{-9}
1.345		7.94×10^{-6}	2.76×10^{-9}	2.91×10^{-9}
1.420	5.52×10^{-6}		1.22×10^{-9}	1.06×10^{-9}
1.495		3.17×10^{-6}	4.48×10^{-10}	3.83×10^{-10}
1.570	8.05×10^{-7}		7.26×10^{-11}	1.39×10^{-10}
1.645		4.53×10^{-7}	2.60×10^{-11}	5.06×10^{-11}
1.720	1.04×10^{-6}		3.79×10^{-11}	1.84×10^{-11}
1.795		5.91×10^{-7}	1.38×10^{-11}	6.68×10^{-12}

(in each run) is a poor predictor of the exact weight function. The other values yield the exact weight function very nicely.

Figure 3 shows plots of the LCAO coefficients and the extracted and exact weight functions (which in the case of the plot are superimposed). The reader should observe that the maximum in the weight function curve is different from the maximum in the LCAO coefficients curve. Moreover, the maximum of the weight functions is shifted to the left, to a region of more diffuse GTOs. Consequently, diffuse functions in a basis set seem to be more important than can be inferred, in a first glance, from LCAO calculations. Besides, one can now clearly see that there is less information in plotting LCAO coefficients as functions of Ω because what would be obtained is dependent on the choice of the basis set used and would belong to that specific calculation.

4 LCAO-SCF calculations are integrations in ζ space

The quadrature interpretation has been previously recognized as approximating an integral equation by a set of linear homogeneous equations in the course of solving

Table 2. Extraction of the weight function from linear coefficients obtained from a Gauss-Lobatto derived basis set.

x	Ω	ζ	C	w	$F_{extracted}$	F_{exact}	$\frac{F_{exact}}{F_{extracted}}$
-1.00	-0.500	4.98×10^{-1}	2.15×10^{-3}	2.78×10^{-2}	2.59×10^{-1}	1.26	4.86
-9.00×10^{-1}	-0.400	9.09×10^{-2}	3.40×10^{-1}	1.65×10^{-1}	3.77	3.14	0.83
-6.77×10^{-1}	-0.177	3.45×10^{-1}	6.37×10^{-1}	2.75×10^{-1}	1.12	1.18	1.06
-3.63×10^{-1}	0.137	2.27	1.50×10^{-1}	3.46×10^{-1}	3.18×10^{-2}	3.15×10^{-2}	0.99
0.00	0.500	2.01×10	1.14×10^{-2}	3.72×10^{-1}	2.54×10^{-4}	2.58×10^{-4}	1.02
3.62×10^{-1}	0.863	1.77×10^{2}	7.22×10^{-4}	3.46×10^{-1}	1.96×10^{-6}	1.94×10^{-6}	0.99
6.77×10^{-1}	1.177	1.17×10^{3}	5.25×10^{-5}	2.75×10^{-1}	2.73×10^{-8}	2.80×10^{-8}	1.03
9.00×10^{-1}	1.400	4.44×10^{3}	3.15×10^{-6}	1.65×10^{-1}	7.14×10^{-10}	1.39×10^{-9}	1.95
1.00	1.500	8.10×10^{3}	5.95×10^{-6}	2.78×10^{-2}	3.67×10^{-9}	3.58×10^{-10}	0.10

x: abscissae of the Gauss-Lobatto quadrature.
Ω: generator coordinate in the range of -0.5 to $+1.5$ obtained from x.
ζ: obtained from Ω through $\zeta = \exp(A\Omega)$, $A = 6.0$.
$F_{extracted}$: extracted weight function according to equation (20).
F_{exact}: exact weight function, equation (19).

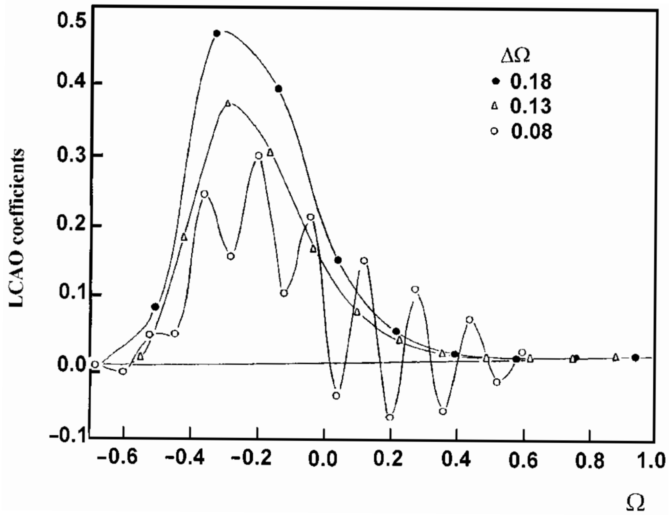

Fig. 2. Hydrogen atom ground state case: plots of LCAO coefficients as functions of Ω for three calculations each using 17 GTOs with different values of $\Delta\Omega$.

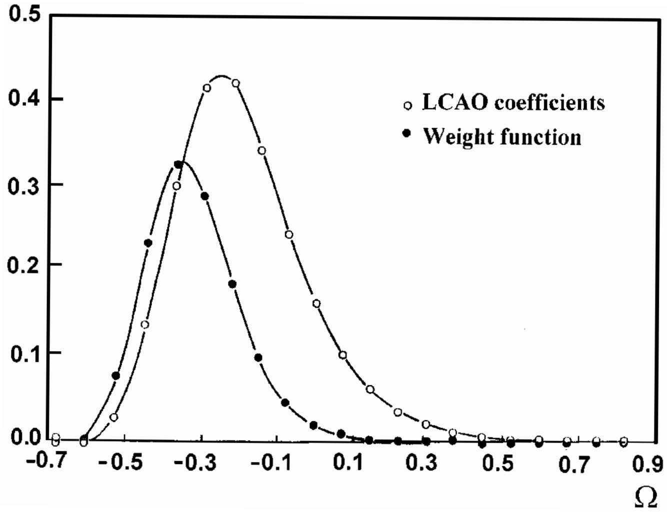

Fig. 3. Hydrogen atom ground state case: plots of LCAO coefficients and of the weight function as functions of Ω.

atomic problems [11–14] (they have considered the integral equation in the context of the Griffin-Hill-Wheeler formalism). However, none has so far understood the problem the other way around, *i.e.*, interpreted the LCAO Roothaan Hartree-Fock formalism as being a quadrature approximation to an implicit integral equation problem as we do here.

In order to provide support to our point that a LCAO calculation is always a quadrature approximation to an implicit integral equation, we shall extract the weight functions from a basis set originated from an explicit quadrature. The hydrogen 1*s* orbital represented by a Gaussian function will again be used as a test case.

By choosing as integration interval in Ω the range from $\Omega = -0.5$ to $\Omega = 1.5$ and sampling this interval with a suitable linear transformation of the abscissae from a 9-point Gauss-Lobatto quadrature [15] which is defined from -1 to 1, we obtained a nine GTO basis set. The linear coefficients obtained after the SCF calculation can then be transformed into the weight function by using

$$F_{i,n}(\zeta_t) = \frac{C_{i,n,t}}{h w_i A e^{A\Omega_t}}, \tag{20}$$

where $h = [1.5 - (-0.5)]/2 = 1$ and w_i are weights of the Gauss-Lobatto quadrature. Table 2 shows results where one can see that the predicted weight function is indeed similar to the exact one, except for the end points.

5 Conclusions

The interpretation that every LCAO calculation is actually performing numerical integration of the generator coordinate Griffin-Wheeler equation is advanced. Exponents of the basis sets are therefore abscissae of the implicit quadrature used in the integration, whereas the linear coefficients automatically incorporate the corresponding weights. We were then able to extract from the LCAO coefficients the weight function, a characteristic of the physical system under study and not of a particular calculation.

Basis set design now becomes a matter of knowing the weight function for the particular problem and of sampling it such that the error in equation (10) becomes minimized. Consequently, either universal or adapted basis sets to a particular physical system can then be created based on wavefunction and density criteria and not only on the energy criterion alone.

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