

Towards an accurate representation of the continuum in calculations of electron, positron and laser field interactions with molecules

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Abstract. Gaussian-type orbitals (GTOs) are the most common choice of basis functions in calculations of electronic structure of molecules, i.e. for the description of bound electrons. The main advantage of this approach is the analytic form of the multicentre molecular integrals. For the same reason GTOs have been adopted as basis functions for the description of the unbound particle in many ab-initio calculations of electron, positron and laser fields interacting with molecules. However, the accurate description of the unbound particle using GTOs may become very difficult and in some cases numerically unstable. We describe an approach for the representation of the continuum in which the unbound particle is described using a mixed GTO and B-spline basis set in a manner which exploits the best features of these functions. Analytical expressions for the GTO-only molecular integrals allow us to accurately represent the part of the wavefunction close to the target, while the B-splines enable us to represent accurately the wavefunction's tail, corresponding to the unbound particle, over a wide range of kinetic energies. The main challenge posed by this approach is the accurate and rapid numerical evaluation of a large number of mixed BTO/GTO molecular integrals. We propose a scheme for this integral calculation in which the overlap integrals between GTOs and B-spline functions play a central role and demonstrate that they can be calculated rapidly and accurately.

1. Introduction

Ab-initio methods for studying molecular processes involving an unbound particle, such as the R-matrix method [1], rely on the use of Gaussian-type orbitals (GTOs) for the description of both the bound electrons of the molecule and the unbound particle (continuum). The central object of the R-matrix method is the R-matrix sphere whose radius must be chosen large enough to fully contain charge density of the molecule. The use of GTOs for the description of the continuum (i.e. the unbound particle) becomes inaccurate or fails completely when large R-matrix radii are needed or when high incident electron energies are required [2].

The origin of the problems in the representation of the continuum using center-of-mass GTOs lies in the need to use functions with very diffuse exponents to guarantee that the resulting continuum orbitals span the whole R-matrix sphere and are non-zero on the boundary. Consequently, the orthogonal continuum orbitals (given as linear combinations of the GTOs) can contain large coefficients and interchanging signs. The combination of those two effects may result in loss of precision of the transformed integrals with obvious consequences for precision of the eigenvalues of the Hamiltonian.



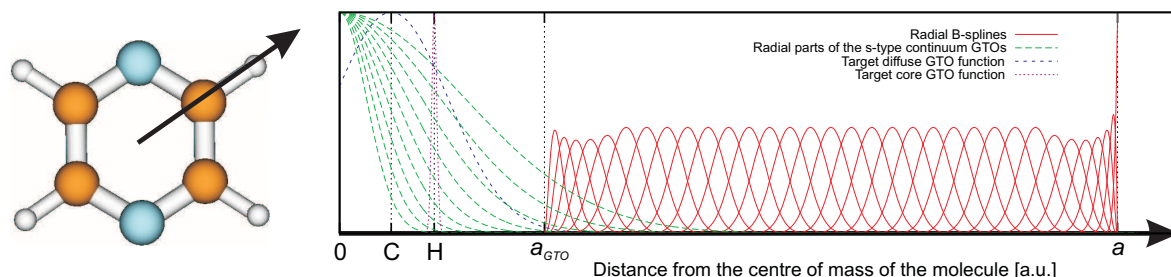


Figure 1. On the left: the target molecule (pyrazine in this case). The black arrow defines the radial coordinate for the figure on the right hand side. On the right: the R-matrix sphere has radius $r = a$ and coincides with the endpoint of the last radial B-spline. The radius for which the continuum GTOs have been optimized is denoted as a_{GTO} . The continuum radial GTOs and B-splines are shown in green and red. The blue curve corresponds to a cross section through a diffuse target GTO centered on the carbon atom. A compact core GTO function centered on the hydrogen is shown in pink.

We propose a new (hybrid) approach for the representation of the continuum which aims to improve significantly its quality and allow large R-matrix radii ($\approx 30 - 50 a_0$) to be used. The method builds on the successful use of B-splines in calculations of unbound processes involving atoms [3, 4] and on the recent breakthrough [5, 6, 7] in calculations of two-electron molecular integrals.

The method requires the use of basis functions of two types: standard GTOs and functions whose radial parts are the B-spline functions (see [4] for a detailed description of B-splines). Consequently, the main challenge posed by this approach is the calculation of the required types of molecular integrals in the mixed GTO/B-spline orbital basis. This work presents results of calculations of the overlap and kinetic energy integrals in the mixed basis and proposes a framework for calculation of the rest of the mixed one- and two-electron molecular integrals.

2. The choice of the continuum basis

Figure 1 illustrates concisely our approach for the representation of the continuum. The R-matrix radius a is chosen large enough to fully contain the molecule's atomic basis functions (more precisely the molecular orbitals). This radius is determined by the spatial extent of the most diffuse target GTOs. However, the atomic core and polarization functions usually have a smaller spatial extent and can be fitted inside a sphere with the radius $a_{GTO} < a$. This sphere will always contain only GTOs and therefore we call it the *GTO sphere*. Based on this observation we construct the continuum basis from two types of functions:

- **GTOs centered on the center of mass (CMS)** of the molecule and optimized for use with the radius a_{GTO} . These functions are generally nonzero inside the whole R-matrix sphere: $r \in [0, a]$.
- **B-spline orbitals (BTOs) centered on the CMS** which span *only* the radial range: $r \in [a_{GTO}, a]$. (The exact form of these functions is defined in Appendix A).

Consequently, the only basis functions which are non-zero in the region outside the GTO sphere are the BTOs, continuum GTOs and some target (usually diffuse) GTOs. This *hybrid approach for representation of the continuum* has several important properties:

- The quality of representation of the continuum inside the GTO sphere is given by the choice of the continuum GTOs. We can control the quality of the continuum inside the GTO sphere by changing its radius (and/or the corresponding continuum GTOs) [8].

- The product of a BTO and those target GTOs fully enclosed by the GTO sphere is identically zero. The product of a BTO and the remaining GTOs is generally non-zero.

These properties may be used to achieve significant savings in the computational cost of calculating the mixed GTO/BTO molecular integrals. The most computationally demanding part of the calculation are the mixed BTO/GTO two-electron integrals:

$$\langle \phi_1 | r_{12}^{-1} | \phi_2 \rangle = \int d\mathbf{r}_1 \int d\mathbf{r}_2 a(\mathbf{r}_1) b(\mathbf{r}_1) r_{12}^{-1} c(\mathbf{r}_2) d(\mathbf{r}_2), \quad (1)$$

$$\phi_1(\mathbf{r}_1) = a(\mathbf{r}_1) b(\mathbf{r}_1), \quad \phi_2(\mathbf{r}_2) = c(\mathbf{r}_2) d(\mathbf{r}_2), \quad (2)$$

where at least one of $a(\mathbf{r}_1)$, $b(\mathbf{r}_1)$ and/or $c(\mathbf{r}_2)$, $d(\mathbf{r}_2)$ is a BTO and the rest of the functions are GTOs. Utilizing the properties listed above these integrals can be split into three classes:

- Identically zero two-electron integrals. This class contains integrals in which at least one of the densities ($\phi_1(\mathbf{r}_1)$ and/or $\phi_2(\mathbf{r}_2)$) contains the product of a BTO and a GTO fully enclosed by the GTO sphere.
- The densities $\phi_1(\mathbf{r}_1)$ and $\phi_2(\mathbf{r}_2)$ are spatially separated. This situation arises when e.g. the density $\phi_1(\mathbf{r}_1)$ involves at least one GTO which is fully enclosed by the GTO sphere while the density $\phi_2(\mathbf{r}_2)$ involves the product of a BTO with a GTO that is non-zero outside the GTO sphere.
- The densities $\phi_1(\mathbf{r}_1)$ and $\phi_2(\mathbf{r}_2)$ spatially overlap, i.e. they both involve products of functions that are non-zero outside the GTO sphere.

Depending on the choice of a_{GTO} we can determine which target functions are fully enclosed by the GTO sphere and therefore assign each two-electron integral into one of the three classes. Class (ii) integrals can be calculated using the multipole expansion of the Coulomb interaction [9]. The most difficult case are the class (iii) integrals. To calculate them we suggest using the method based on resolution of the Coulomb operator into single-particle functions [7] centered on the CMS:

$$r_{12}^{-1} \approx \sum_{k=1}^n \psi_k(\mathbf{r}_1) \psi_k(\mathbf{r}_2) \rightarrow \langle \phi_1 | r_{12}^{-1} | \phi_2 \rangle \approx \sum_{k=1}^n \langle \phi_1 | \psi_k \rangle \langle \phi_2 | \psi_k \rangle. \quad (3)$$

The same approach can be used to calculate the mixed one electron nuclear attraction integrals. We can see that the calculation of the mixed GTO/BTO overlap integrals plays a crucial role in the suggested approach.

3. Interaction-free electron scattering

As the first step towards implementing the proposed approach for the representation of the continuum we calculated the mixed GTO/BTO overlap and kinetic energy integrals utilizing the CMS-centered partial wave expansion of the GTO. Formulae for these integrals can be found in Appendix A. In order to test the approach on a realistic system we solved, using the R-matrix method, the one-electron free potential scattering problem. In order to solve this problem we also needed the GTO/GTO and BTO/BTO overlap and kinetic energy integrals whose evaluation is trivial.

To mimic the description of the continuum electron in the R-matrix suite the set of orbitals used were those of the continuum and the Hartree-Fock (HF) molecular orbitals of two selected molecules: water and pyrazine. In order to obtain a set of orthogonal orbitals we utilized the standard procedure used in the molecular R-matrix calculations: the HF (orthogonal) orbitals were kept unchanged throughout the calculation. Orbitals based on the CMS continuum GTOs and BTOs were first Schmidt orthogonalized to the target orbitals and then symmetrically

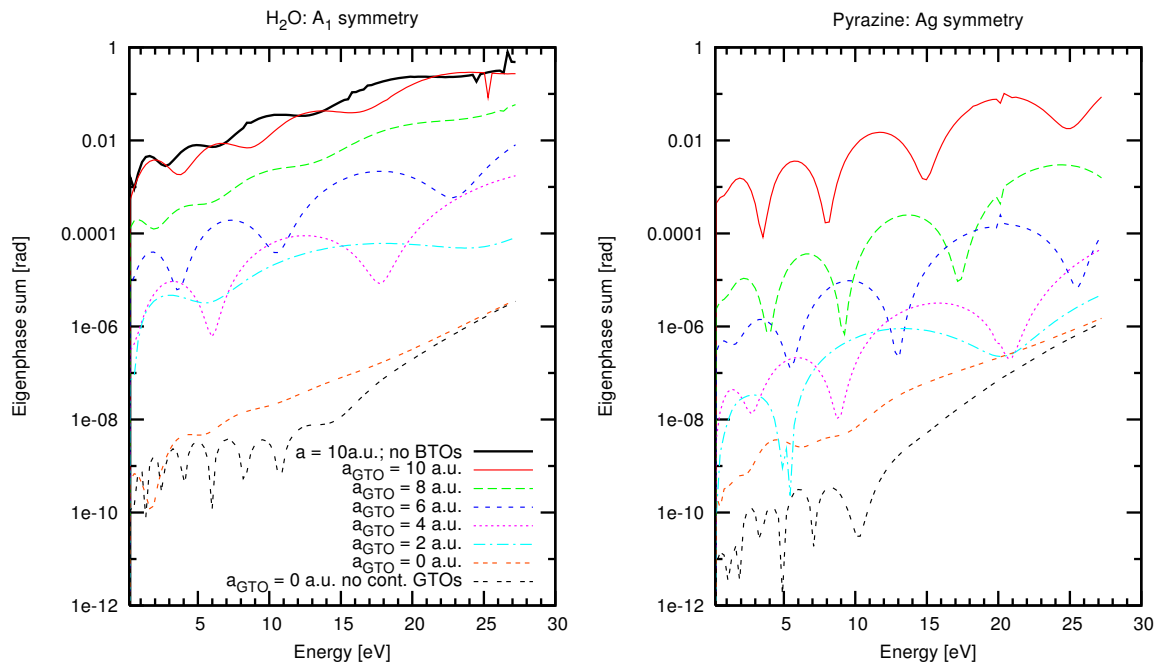


Figure 2. Eigenphase sums for interaction-free scattering from water (C_{2v} symmetry) and pyrazine (D_{2h} symmetry) for the totally symmetric contribution. The exact eigenphase sum is zero. The colour lines are for results when both the GTOs and BTOs were used; the starting radius for the BTOs (a_{GTO}) is indicated in the Figure.

orthogonalized among themselves. Finally, all continuum orbitals with eigenvalues of the continuum-continuum overlap matrix smaller than 10^{-7} were deleted. In all calculations we used the same continuum GTO basis optimized for a radius $a_{GTO} = 10a_0$. The BTO radial basis consisted of B-splines of order 8 with break points separated by $1 a_0$ and spanning the radial distance of $29a_0$. This set of radial B-splines was kept fixed and only translated along the radial coordinate according to the value of a_{GTO} . For water (pyrazine) an R-matrix radius a of $10a_0$ ($18a_0$) was sufficient to enclose all target orbitals.

Figure 2 shows the results obtained when the target orbitals were those of water (6 orbitals of A_1 symmetry) and pyrazine (14 orbitals of A_g symmetry). We show only the results obtained for scattering in the totally symmetric irreducible representation; results for the rest of the symmetries were similar. For water we show the eigenphase sum obtained when only GTOs (and $a = 10a_0$) were used for the continuum as well as the result obtained when only the BTOs ($a_{GTO} = 0$ and $a = 28a_0$) were used for the continuum. In both cases (water and pyrazine) we observe a rapid and systematic improvement of the quality of representation of the continuum as a_{GTO} decreases, i.e. as the BTOs are pushed closer towards the CMS. Clearly, for $a_{GTO} = 6a_0$ we already obtain eigenphase sums which are for all energies smaller than the value of the smallest eigenphase sum obtained for $a_{GTO} = 10a_0$.

The relative precision of the overlap and the kinetic energy integrals was never worse than 10^{-10} for pyrazine and 10^{-13} for water. As expected based on the properties of the partial wave expansion of the GTO, the relative precision of the integrals generally decreases as the distance of the center of the GTO from the CMS is increased and as the angular momentum and exponent of the GTO are increased. The only numerical problems (loss of precision) were detected during the integral transformation step; we are currently investigating possible resolutions of this problem.

The calculation of the mixed GTO/BTO integrals utilized the point group symmetries of the target molecules and in both cases took ≈ 9.7 s on an Intel Xeon 2.50 GHz workstation.

4. Conclusions

We propose and test a methodology for a hybrid GTO/BTO representation of the continuum that can be used for calculations of electron, positron and light interactions with molecules. This approach was found to be much more accurate than our currently employed GTO-only approach. We showed that the mixed GTO/BTO overlap and kinetic energy integrals can be calculated accurately and efficiently. Somewhat surprisingly we found that the most serious numerical problem is the loss of precision that may occur on the level of the integral transformation. The numerical stability of the mixed BTO/GTO primitive overlap and kinetic energy integral calculation can be controlled for and does not appear to cause significant problems.

Appendix A. Overlap and kinetic energy integrals between GTOs and BTOs

We use GTOs in the standard form:

$$\chi_{\alpha LM}(\mathbf{r} - \mathbf{R}) = N_{\alpha L}^{GTO} S_{LM}(\mathbf{r} - \mathbf{R}) \exp[-\alpha|\mathbf{r} - \mathbf{R}|^2], \quad N_{\alpha L}^{GTO} = \sqrt{\frac{2(2\alpha)^{L+3/2}}{\Gamma[L+3/2]}} \frac{2L+1}{4\pi}, \quad (\text{A.1})$$

where \mathbf{R} is the radius vector pointing in the direction of the centre of the GTO, α is the exponent of the GTO and L, M describe the angular dependence of the GTO through the normalized real solid harmonics $S_{LM}(\mathbf{r} - \mathbf{R})$ centered at $\mathbf{r} = \mathbf{R}$. We follow the standard conventions [10] for the definition of the real solid harmonics. The normalization factor $N_{\alpha L}^{GTO}$ is chosen to reproduce the unit self-overlap of the GTO. The B-spline orbital centered on the center of mass of the molecule (BTO) is defined by the equation:

$$\mathcal{B}_{L_i M_i}^i(\mathbf{r}) = N_i^{BTO} \frac{B_i(r)}{r} X_{L_i M_i}(\hat{\mathbf{r}}), \quad N_i^{BTO} = \left[\int_{t_i}^{t_{i+k}} dr (B_i(r))^2 \right], \quad (\text{A.2})$$

where $X_{L_i M_i}(\hat{\mathbf{r}})$ is the normalized real spherical harmonic [11], r is the distance from the origin, N_i^{BTO} is the normalization factor chosen to reproduce the unit self-overlap of the BTO and $B_i(r)$ is the B-spline function in coordinate r (piecewise polynomial with compact support); t_i, \dots, t_{i+k} is the set of $k+1$ knots, where $k > 0$ is the order of the B-splines (see [4] for details).

The overlap integral between a GTO (not centered on the CMS) and a BTO is given *exactly* by a finite sum of terms originating in the partial wave expansion of the GTO [12] and has the form:

$$\begin{aligned} \langle \chi_{\alpha LM} | \mathcal{B}_{L_i M_i}^i \rangle &= \frac{4\pi}{\sqrt{\alpha R(2L+1)}} N_i^{BTO} N_{\alpha L}^{GTO} \sum_{j=1}^{n_{LM}} d_j^{LM} (-1)^{\mu_j + l'_j + m'_j} \mathcal{I}_{\lambda_j \mu_j} \mathcal{I}_{\lambda'_j \mu'_j} R_{l'_j}^{l'_j} X_{l'_j m'_j}(\hat{\mathbf{R}}) \times \\ &\times \sum_{l=l_{\min}}^{l_{\max}} R_{i, \lambda_j, l}(\alpha, R) \sum_{m=-l}^l \langle L_i M_i | \lambda_j \mu_j | l m \rangle_R X_{lm}(\hat{\mathbf{R}}), \end{aligned} \quad (\text{A.3})$$

where d_j^{LM} are coefficients in the translation formula [13] for the real unnormalized solid harmonics $z_{LM}(\mathbf{r}_1 + \mathbf{r}_2)$:

$$z_{LM}(\mathbf{r}_1 + \mathbf{r}_2) = \sum_{j=1}^{n_{LM}} d_j^{LM} z_{l_j m_j}(\mathbf{r}_1) z_{l'_j m'_j}(\mathbf{r}_2), \quad (\text{A.4})$$

$$z_{LM}(\mathbf{r}) = (-1)^M \mathcal{I}_{LM} r^L X_{LM}(\hat{\mathbf{r}}), \quad \mathcal{I}_{LM} = \sqrt{\frac{2\pi(1 + \delta_{M,0})}{2L+1}} \frac{(L+|M|)!}{(L-|M|)!}, \quad (\text{A.5})$$

$\langle L_i M_i | \lambda_j \mu_j | l m \rangle_R$ are the Gaunt coefficients for the real spherical harmonics and

$$R_{i,\lambda_j,l}(\alpha, R) = \int_{t_i}^{t_{i+k}} dr B_i(r) r^{\lambda_j+1/2} \exp[-\alpha(r-R)^2] \tilde{I}_{l+1/2}(2\alpha r R) \quad (\text{A.6})$$

are the radial integrals in which $\tilde{I}_{l+1/2}(2\alpha r R) = \exp[-2\alpha r R] I_{l+1/2}(2\alpha r R)$ stands for the exponentially scaled modified Bessel function. These radial integrals are obtained using an adaptive numerical quadrature. In order to speed up the calculation we use recurrent relations for $R_{i,\lambda_j,l}(\alpha, R)$ which (for fixed i, α and R) couple the λ and l parameters:

$$R_{i,\lambda,l-1}(\alpha, R) = R_{i,\lambda,l+1}(\alpha, R) + \frac{l+1/2}{\alpha R} R_{i,\lambda-1,l}(\alpha, R). \quad (\text{A.7})$$

These recurrent relations can be derived using the well-known downward (numerically stable) recurrent relation for the modified Bessel functions $I_{l+1/2}(x)$. The formula for the kinetic energy integral $\langle \chi_{\alpha LM} | \Delta | \mathcal{B}_{L_i M_i}^i \rangle$ retains the same form as (A.3) with exception of the radial integral which has the form:

$$\begin{aligned} R_{i,\lambda_j,l}^{\Delta}(\alpha, R) &= \int_{t_i}^{t_{i+k}} dr B_i''(r) r^{\lambda_j+1/2} \exp[-\alpha(r-R)^2] \tilde{I}_{l+1/2}(2\alpha r R) - \\ &- L_i(L_i+1) R_{i,\lambda_j-2,l}(\alpha, R), \end{aligned} \quad (\text{A.8})$$

where $B_i''(r)$ stands for the second derivative of the B-spline $B_i(r)$. The relative precision of the individual terms entering (A.3) is not lower than $\approx 10^{-14}$ and the only loss of precision may occur as a result of subtraction of competing partial-waves when the overlap (or the kinetic energy) integral is close to zero due to symmetry. However, the occurrence of these instabilities can be mitigated by the choice of the breakpoint sequence for the radial B-splines which destroys the spatial symmetry of the integrand $\chi_{\alpha LM}(\mathbf{r}-\mathbf{R}) \mathcal{B}_{L_i M_i}^i(\mathbf{r})$. Other means by which the calculation can be stabilized are being investigated.

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