Spherical tensor gradient operator method for integral rotation: A simple, efficient, and extendable alternative to Slater–Koster tables

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Electronic structure methods require the evaluation of an enormous number of integrals, and before the widespread availability of powerful computers, it was often necessary to circumvent their explicit calculation. "Tight-binding" models were popularized long ago because they construct approximate Hamiltonians that require only two-center integrals;[1] however, the tremendous computational advantage of these models still make them the method of choice for applications that push the boundaries of the nano- and mesoscale regimes.[2] There has been a recent resurgence of interest and effort toward improving the accuracy and robustness of tight-binding models and extending the scope of their applications to include molecular simulations of biological macromolecules in realistic environments.[3,4] In this paper, we present a novel advancement in the mathematical treatment of the integrals and integral gradients used in these models based on a spherical tensor gradient operator (STGO) formulation. The STGO method will allow for the efficient evaluation of atomic forces in large systems and is easily extended to high angular momentum basis functions.

The speed of tight-binding models is achieved, in part, by pretabulating the two-center integrals on cubic splines. These splines can then be used during molecular simulations to avoid the costly overhead of recalculating the integrals at each time step. Spherical harmonics are used to describe the angular dependence of the basis functions, and their symmetry properties can be exploited to reduce the volume of precomputed data. When aligned along the z-axis, most of the two-center integrals vanish, and many of the remaining integrals become redundant.[5] The interpolated integral matrices must be rotated by Euler angles when the atoms are not aligned along the z-axis. Symbolically carrying out these rotation transformations yields a series of equations referred to as the Slater–Koster tables (SKTs). These equations express the matrix elements in the rotated frame with direction cosine polynomials and the integrals in the z-axis oriented frame (referred to here as the Slater–Koster parameters). Early attempts to publish the SKTs for high angular momentum ($l>2$) functions were incomplete or riddled with errors because of the large number of resulting equations.[6,7] The derivatives of these expressions, required to obtain the forces in molecular simulations,[8] are even more complicated. To address the practical problem of properly implementing the $l>2$ SKTs, it has been suggested that they be generated using automated procedures.[9] For example, by use of the MATHEMATICA (Ref. 10) program[11,12] or by factoring the direction cosines into polynomials of lower order.[13] The present note provides a simple alternative method that improves the efficiency of high angular momentum basis function integral and gradient evaluation.

We recently reported[14] a method that used the STGO to derive expressions for the efficient evaluation of two-center multipolar Gaussian integrals and gradients. We showed that the only dependence of the expressions on the primitive exponents and contraction coefficients was through an "auxiliary vector." In this note we show that for $R_{ab}>0$, there exists a unique mapping by means of inverting a nonsingular square matrix between the Slater–Koster parameters and the required elements of the auxiliary vector. This transformation then allows one to exploit the efficiency afforded by the STGO formulation. One can interpret this as performing an exact fit of a numerical basis with primitive Gaussian functions; however, the direct determination of the auxiliary vector bypasses the need for explicitly determining any primitive quantities. The method borne from this uses splines of the auxiliary vector elements, as opposed to the Slater–Koster parameters, and then uses the integral and derivative expressions presented in Ref. 14 (the notation for which will be adopted henceforth), as opposed to the SKTs.

To demonstrate the relationship between the Slater–Koster parameters and the auxiliary vector, consider the $(2l_a+1)(2l_b+1)$ matrix of integrals when the two atoms are positioned along the z-axis $\mathbf{R}_{ab}\rightarrow\mathbf{z}_{ab}$, and let us assume, without loss in generality that $l_a\geqslant l_b$. There are then only l_b+1 unique nonzero integrals (Slater–Koster parameters) corresponding to equal cosine components of the harmonics, i.e., $\mu_a=\mu_b=\mu\geqslant 0$, and these values can be packed into a vector, whose elements $(0\leqslant\mu\leqslant l_b)$ are given by

$$\begin{pmatrix} l_a \\ \mu \end{vmatrix} O \begin{vmatrix} l_b \\ \mu \end{pmatrix} = \sum_{j=0}^{l_b} \begin{pmatrix} 0 \\ 0 \end{vmatrix} O \begin{vmatrix} 0 \\ 0 \end{pmatrix}^{(l_a+l_b-j)} \Omega_{j,\mu}, \tag{1}$$

where

$$\Omega_{j,\mu} = \frac{(-1)^{l_b} 2^{l_a+l_b-j}(2j-1)!!}{(2l_a-1)!!(2l_b-1)!!} \times \sum_{\kappa=-j}^{j} \tilde{W}_{(l_a,\mu),(j,\kappa)}(\mathbf{z}_{ab}) \tilde{W}_{(l_b,\mu),(j,\kappa)}(\mathbf{z}_{ab}). \tag{2}$$

Equation (1) references only l_b+1 elements of the auxiliary vector, and these elements are used exclusively even when the atoms are arbitrarily oriented. We therefore refer to this as the segmented basis auxiliary vector, the elements of which can be determined from the Slater–Koster parameters

TABLE I. Comparison of SKT and GY timings (microseconds). L is the angular momentum of the functions, which have been chosen to be identical for the purposes of tabulation. The computer code was written in FORTRAN 95 and compiled with the Intel FORTRAN COMPILER Version 10.0 with the options -arch sse2 -tune pn4 -xN -static -O3, and timings were performed on an Intel Pentium 4 2.4 GHz processor with 512 kbytes of cache and 1 Gbyte of random access memory.

	Integrals			Derivatives		
L	SKT	GY	Ratio	SKT	GY	Ratio
2	0.31	0.29	1.1	1.30	0.45	2.9
3	0.90	0.57	1.6	5.05	1.47	3.4
4	1.98	1.24	1.6	13.86	3.19	4.3
5	4.31	2.36	1.8	49.90	7.46	6.7

by inverting the Ω matrix. In the particular case of $R_{ab}=0$, the integrals $l_a \neq l_b$ are zero by the orthogonality of spherical harmonics, and therefore any auxiliary vector would be valid. Given the segmented auxiliary vector, the calculation of the integrals follows trivially from Ref. 14.

To compute the gradients from the equations presented in Ref. 14, one must obtain the l_a+l_b+1 element of the auxiliary vector. If the auxiliary vector elements are stored as a cubic spline,[15] then their derivatives d/dR_{ab} are readily available, and thus

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} |O| \begin{pmatrix} 0 \\ 0 \end{pmatrix}^{(l_a+l_b+1)} = \frac{1}{2R_{ab}} \frac{d}{dR_{ab}} \begin{pmatrix} 0 \\ 0 \end{pmatrix} |O| \begin{pmatrix} 0 \\ 0 \end{pmatrix}^{(l_a+l_b)}. \tag{3}$$

Alternatively, one can compute it from finite differentiation of the l_a+l_b element and include it as an additional spline.

Table I compares the integral and derivative timings using the present method (denoted GY) and the SKTs. To make a comparison we generated[16] the SKTs from Ref. 11 (we found similar results using Ref. 12) and evaluated the derivatives from elementary chain relations. Further optimization of both source codes is possible; however, the main goal in treating arbitrary angular momentum is to automate a procedure that removes the difficulty and errors prone to hand optimization of a very large number of complicated equations. Ultimately, the assessment of performance is best evaluated by implementation within the framework of the particular quantum model of interest. For example, if electrostatics are treated with Gaussian multipole expansions, then the commonality of the expressions resulting from the STGO formulation can be exploited. Table I is a simple comparison used to demonstrate that the GY method easily extends to high angular momentum, and evaluates the gradients three to four times faster than elementary differentiation of the SKTs. The efficiency of the GY gradients result from having expressed the derivatives in each Cartesian direction with a common set of auxiliary integrals.

The present method is novel in that it recasts the problem into an exact, yet implicit, basis representation through which the properties of the STGO can be exploited. The result is a simple and efficient alternative to the SKTs that achieves improved performance for arbitrary angular momentum basis function integral and gradient evaluation.

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[15] Cubic spline interpolation errors of the (l_a+l_b-j)th auxiliary vector element can be minimized through scaling of the element by $R_{ab}^{l_a+l_b-2j}$ when constructing the spline and then dividing by this factor upon spline lookup. This scale factor derives from the homogeneity properties of the solid harmonics, and the scaled elements correspond to those obtained by inverting the Ω matrix using unit separation along the z-axis.
[16] The SKT computer code is written in FORTRAN 95, which was generated from the MATHEMATICA program, optimized using the FullSimplify command and further manipulated by replacing direction cosine polynomials with variables, which could be computed once.