CHIRALEX: theory

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(Dated: January 24, 2022)

I. INTRODUCTION

Essential parameters are kept in the *params* dictionary, which is passed throughout the program. It is used to construct all types of objects, from grids to the propagator object.

II. BASIS FUNCTIONS AND GRIDS

A. Radial quadratures

B. Radial grid

The radial grid used to solve the TDSE is based on an underlying Gauss-Lobatto (GL) quadrature scheme. First, a generic quadrature grid is created: $\{x_k\}_{k=0,1,...,Nlobs-1} \in [-1,1]$. Its size is determined by the *Nlobs* input parameter (Nl for short notation). Note that the boundary points in the Gauss-Lobatto grid are -1 and $+1$. The GL grid is then scaled to reflect the bin size R_b requested by the user (*binw* input parameter):

$$S_k = \frac{1}{2} R_b \, (x_k + 1) \tag{1}$$

Bin size must be determined empirically to ensure good convergence and stability of the results. Next, the scaled grid is copied and translated by the bin size to generate the full primitive radial grid G_{prim}:

$$r_{ik} = S_k + T_i, \qquad i = 0, 1, ..., Nb-1 \, , k = 0, 1, ..., Nlobs-1 \tag{2}$$

where $T_i = i \cdot R_b + \epsilon$. The constant shift ϵ (rshift keyword) is optional and by default is set to 0. The resulting grid has the size $Nb \times Nlobs$ and contains boundary points $r_{00} = \epsilon$ and $r_{Nb-1,Nlobs-1} = R_{max}$. The last point from bin i and the first point from bin $i+1$ are identical in the primitive grid.

The *coupled grid* G is generated by removing boundary points, plus merging duplicate points at bin boundaries in G_{prim}. Through these operations the size of the coupled grid is $Nr = Nb \times (Nlobs - 1) - 1$. Note that all indices start from 0 for python compatibility. For example $G_{00} = r_{01}$ and $G_{0,Nl-3} = r_{0,Nl-2}$. The boundary of the first bin is at $G_{0,Nl-2} = r_{0,Nl-1} = r_{10}$. The last point in the coupled grid is $G_{Nb-1,Nl-3} = r_{Nb-1,Nl-2}$.

C. Radial basis functions

1. *Interpolated radial functions*

D. Angular basis functions

III. INDEX MAPPING

A natural choice for mapping the basis set indices is to set the grid points as major dimension (changing last). Such a choice offers a simple way of cutting the Hamiltonian matrix at a given grid point by slicing the basis. We name this convention as 'DVR' mapping. Bridge functions, as discussed in II B, are defined for indices $n = Nl - 2$, that is the last index in each bin. A consequence of such a choice is a near block-diagonal structure of the Hamiltonian. Another common choice is to choose bridge functions as first in the bin ($n = 0$), which results in 'arms' reaching out from bin i into bin $i+1$, as shown in **??**. Another option given in the code is to select mapping in which the angular quantum numbers l, m are the major dimension. We name this convention 'SPECTRAL'. The choice for mapping is determined by the 'map_type' = 'DVR,SPECT' keyword. With the 'DVR' convention the map is given as follows:

$$p(i,n,l,m) = (i \cdot (Nl-1) + n) \cdot (l_{max}+1)^2 + l \cdot (l+1) + m \tag{3}$$

with $p(0,0,0,0) = 0$. For $l_{max} = 0$ we have $p(Nb - 1, Nl - 3, 0, 0) = Nb \times (Nl - 1) - 2$, which retrieves the size of the coupled radial grid/basis set. The map is stored in a numpy array ('maparray') and is saved in file. The ranges for the radial indices i and n are the same as for the coupled grid, i.e. $i = 0, 1, 2, ...Nb - 1$ and $n = 0, 1, 2, ..., Nl - 2$ for $i < Nb - 1$ and $n = 0, 1, 2, ..., Nl - 3$ for $i = Nb - 1$.

IV. ROTATED ELECTROSTATIC POTENTIAL

Each molecular-frame orientation gives different electrostatic potential as seen from the laboratory frame, in which the basis set is defined. This means that for each orientation one must generate generally a different Lebedev quadrature grid. Even if a global scheme is used,

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TABLE I. Example 'DVR' coupled basis set index mapping for $Nb = 3$, $Nl = 3$, $lmax = 1$.

i	n	ξ	l	m	p
0	0	0	0	0	0
0	0	0	1	-1	1
0	0	0	1	0	2
0	0	0	1	+1	3
0	1	1	0	0	4
0	1	1	1	-1	5
0	1	1	1	0	6
0	1	1	1	+1	7
...					
2	0	4	1	0	18
2	0	4	1	+1	19

the values of the electrostatic potential will be different at these points for each orientation. This is because the lebedev grid is defined in the laboratory frame. Therefore at this stage, a separate Psi4 calculation must be initialized for each orientation. I do not see a way around it at the moment, other than performing multipole expansion and calculating the angular part (spherical tensor form) of the potential analytically. But finding this expansion is costly, even more than running Psi4 for every orientation.

V. KINETIC ENERGY OPERATOR

VI. HAMILTONIAN

We decided to keep the bound state Hamiltonian H_0 and the initial propagation Hamiltonian H_{init} as separate entities, calculated independently. The computational overhead related to calculating the bound-state part twice is marginal, as we assume that the full propagation basis is much bigger than the basis for the bound Hamiltonian $Nbas \gg Nbas0$. Future releases might recycle the bound state KEO and POT and build only the outside region Hamiltonian.

VII. WAVEPACKET PROPAGATION

A. time grid

The time grid for the calculation is determined by the input keywords:

The generated grid is equidistant given by the following formula:

$$t[i] = t_0 + i \cdot dt;\ i = 0, 1, 2, ..., Ntpts \tag{4}$$

TABLE II. Time grid keywords.

keyword	description	type
t0	start time	float
tmax	end time	float
dt	time step	float
time_units	units	string
wfn_saverate	save rate of the wavepacket	float

where

$$Ntpts = \left\lceil \frac{t_{max} - t_0}{dt} \right\rceil \tag{5}$$

such that the array of time-points contains elements: $t[0], t[1], ..., t[Ntpts]$. Note that the last point (tmax) is included in the grid.