

# Algorithm for Choosing ABM Parameters

R. T Pack and G. A. Parker

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The following is for reactions with barriers where few, if any, asymptotically closed  $\mathcal{E}$ 's dip down and become locally open in the interaction region. For reactions where potential wells cause many asymptotically closed levels to become locally open, test calculations will be necessary to determine to which asymptote those levels diabatically connect, and enough basis functions included in that arrangement channel to assure their presence and convergence.

- Get the values of  $r_e$ ,  $\omega_e$ , and  $\omega_e x_e$  for the diatomics of all three arrangements from a spectroscopic tabulation such as Huber and Herzberg.
- Determine the largest  $\rho$  to be used from the requirement that all the long range potentials be negligible there compared to scattering energies or accuracies to which resonances are needed.
- Determine accurate values of the vibrational energy levels at this large  $\rho$ . This can be done with abm using a large unoptimized vibrational basis but only the lowest allowed rotational states, or it can be done with the Delves Basis or Jacobi Basis parts of APH3D. If the last of these is used, it will give true asymptotic levels which will lie slightly above the actual levels at any large but finite  $\rho$ .
- Choose maxvib (noscil) to be at least two quanta larger than the largest  $v$  expected to be open at *any*  $\rho$ . This is necessary to maintain completeness in performing the overlaps between sectors.
- Keeping only the lowest allowed rotational state in each arrangement and the same large  $\rho$ , optimize the vibrational energy levels in each arrangement by varying the scaling parameters  $c_\alpha$ ,  $r_x$ , and  $a_n$  cyclically in that order until all are optimum. In doing this, the number of quadrature points, nhermt, must be large enough that the energy levels are stable with respect to it to at least one more significant figure than the accuracy needed for the energy levels. This process goes quickly if one looks at one arrangement at a time with only one basis function in the other arrangement channels. During this, one minimizes the average energy (selected using nave1 and nave2) of all the levels expected to be open anywhere plus one that will be closed everywhere (if possible). If this results in vibrational levels that compare well enough with those determined in step 3

(i.e., to about 0.1 meV), one is done with this step. If not, he must either increase the size of the basis or decrease the number of levels included in the average energy and then reoptimize.

- Choose the  $j_{\max}$  in each arrangement so that all the asymptotically open vibration-rotation states are included.  $j_{\max}$  need usually be no larger than this because the high  $j$  states are repulsive and play little role in the strong interaction region.  $n_{\text{legn}}$  needs to be larger than  $j_{\max}$  at large  $\rho$  and considerably larger than that at small  $\rho$  to keep the channel quadratures converged.
- Estimate the smallest  $\rho$  needed,  $\rho_{\min}$ . That may be obtained from a few dvr, fem or preliminary abm calculations and WKB arguments to assure that the  $\psi(\rho)$  are down to about  $10^{-5}$  their turning point values.
- For each arrangement  $f$ , set  $\rho$  to the larger of  $\rho_{\min}$  and  $s_{mf}$ , the scaled equilibrium distance ( $r_{xf}r_{ef}/d_f$ ). Check to be sure the quadrature to be used there (alternate or channel) gives  $\mathcal{E}$ 's that are solidly converged w/o quadrature and eigenvalues of the primitive overlap matrix that are all positive. Minimize the average over all the open (or low-lying)  $\mathcal{E}$ 's under variations of  $\zeta_f$  and  $\delta_f$  to obtain optimum values of these parameters.
- If the alternate quadrature is necessary to converge the integrals at  $\rho_{\min}$ , choose a reasonable  $\rho_{\text{switch}}$ , which is usually the smallest rho at which the channel quadratures are readily convergable. Check to be sure both quadratures are converged there.
- The parameters  $b_\alpha$ ,  $r_\alpha$ , and  $d_\alpha$  can be used to make  $c_\alpha$  depend on  $\rho$ . That comes in if Old Way = yes is chosen. That is not usually necessary in the current version of the code, and the  $d_\alpha$ 's can be kept equal to zero.
- If one of the channels is much smaller than the other(s) and has a correspondingly tighter quadrature mesh, setting  $\text{intwt}=2$  for that arrangement will cause overlap integrals between basis functions in that channel and those in other channels to be done only in the channel with the better quadrature and may allow use of the channel quadratures at smaller  $\rho$  than otherwise.
- abm leaves out basis functions whose eigenvalue of the overlap matrix is less than  $\text{eigmin}$ . For ordinary double precision arithmetic,  $\text{eigmin}$  should be kept set to 1.e-06. A message is generated if overlaps between two arrangements evaluated by quadratures in the two channels differ by more than  $\text{ovrerr}$ , and 1.e-04 is a convenient value for it.
- $\text{ngood}$  is the number of surface eigenfunctions to be written out. One should set  $\text{nfreq}$  equal to  $\text{ngood}$ . If the number of eigenvalues generated falls below that, the program will stop.

The parameters in Table I of the ABM paper or Table I of the big recent HO2 paper (Prof. Lagana has a copy) are determined from the masses, spectra of the diatomic molecules, and the highest energy you plan to use as in the Algorithm writeup. The only things in Table I which can vary are the numbers of quadrature points, and it is important that you check at several rho to make sure your quadratures are always better converged than your energies.

The parameters  $r_x$ ,  $a_n$ , and  $c_{alpha}$  are always near unity. I start with them equal to unity and then vary them at the largest rho needed, as in step 5 of the Algorithm writeup to find their optimum values for the size basis I am using. They are scaling parameters. The quantities they scale are determined by the program from the input parameters of Table 1, but the scaling parameters are determined totally by optimizing the energy levels at very large rho. In our work thus far, the optimum value for  $r_x$  has turned out to be slightly larger than 1, and the optimum values for  $c_{alpha}$  and  $a_n$  have turned out to be slightly smaller than 1.

During the above calculations, I usually take zeta to be 1 and delta to be 0.01. The calculations at large rho should be rather insensitive to them. Then, I go to the smallest rho at which the ABM calculations will be done and optimize the energies by varying zeta and delta. If your smallest rho is still larger than the  $s_m$  in all of your channels, your results should not depend much on zeta and delta and a rough optimization will suffice. Otherwise, you will have to vary them more carefully. In all this, you need to be careful to be sure your quadratures are still well converged, or the nonlinear least squares minimization (of the average of the N energies you want to be accurate) will converge to values which make the quadratures diverge and give spurious energies.