DeFT Input

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The first line of the input deck is reserved for a descriptive title. If no title is supplied, this line should be left blank. The remaining input deck is keyword-driven. The complete keywords are listed in the following description, but only the first four characters of each need be supplied for the program to perform properly.

"cartesian"

The geometry will specified in cartesian coordinates on the subsequent lines. For each atom, its atomic symbol (optionally followed by a descriptive one or two character label), x, y, and z coordinates must be supplied. The last atom in the system is followed by a line simply stating *"end"*. If the coordinates are in Angstroms, the keyword *"angstroms"* must follow *"cartesian"*. Otherwise, the default, atomic units, is used. Dummy atoms, assigned the atomic symbol xx, may be used.

"zmatrix"

The geometry will be specified with the use of a z-matrix. As with the *"cartesian"* keyword, the default units are atomic units, which again may be overriden by using the *"angstroms"* keyword after *"zmatrix"*. Again, the list of atoms is terminated by a line simply containing *"end"*. In z-matrix format, each atom, i, is listed as follows

$$symbol \qquad i1 \; ri \qquad i2 \; ai \qquad i3 \; di$$

where *symbol* is the atomic symbol of the atom (again, optionally followed by a descriptive one or two character label), ri is the distance between atoms i and $i1$, ai is the value of the angle i–$i1$–$i2$, and di is the value of the dihedral i–$i1$–$i2$–$i3$. The first line need only contain *symbol*, the second, only up to ri, and the third, only up to ai. Dummy atoms, assigned the atomic symbol xx, may be used.

"runtype"

The types of calculation to be performed are listed after this keyword. A minimum of one and a maximum of two keywords must follow *"runtype"*. If an SCF is to be performed from scratch, include the keyword *"start"*. If restarting an SCF, include *"restart"*, rather than *"start"*, after the *"runtype"* keyword. If a geometry optimization is to be performed, include *"optimize"*. If

continuing a geometry optimization, use *"continue"* all alone after *"runtype"*, without any of the other keywords *"start"*, *"restart"*, or *"optimize"*. In this case, the first geometry of this run will be read from the previous run's restart file. Finally, the *"vibrations"* keyword should be alone in following *"runtype"* as well when one wishes to perform a vibrational analysis by finite differentiation of analytic first derivatives. The geometry at which the vibrational analysis is to be performed is read from the restart file of a previously completed geometry optimization run. The default is simply *"start"*, i.e., a single SCF is run from scratch and no geometry optimization is performed.

"potential"

The nature of the functional for the exchange-correlation (XC) energy density and potentials follows this keyword. The default, *"local"*, selects the Vosko-Wilk-Nusair (VWN) local functional (S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980)). Non-local corrections can be selected by following *"potential"* with *"beckeperdew"* instead. This approach uses the Becke nonlocal functional for exchange (A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988)) and the Perdew nonlocal functional for correlation (J. P. Perdew, *Phys. Rev. B* **33**, 8822 (1986)). If one uses the *"mixbeckeperdew"* keyword instead, SCF calculations are performed with the VWN local functional while nonlocal corrections are added perturbatively to the energy and energy gradients. Such calculations make use of the first and second derivatives of the self-consistent local density rather than the self-consistent nonlocal density when calculating the nonlocal corrections.

"grid"

The nature of the grid used in the XC fitting and integration schemes is defined after the *"grid"* keyword. With the *"fine"* option, 832 points per atom are used for the fitting procedures and 2968 for the numerical integrations. With the *"coarse"* option, only 384 and 1708, respectively, are used. If one wishes to randomly orient each sphere of grid points in an attempt to reduce noise in the total energy, the *"random"* keyword should be included on this line. Otherwise, the *"nonrandom"* keyword should be included. This is done primarily when one wishes to conserve symmetry. The default options are *"fine"* and *"random"*. This combination is the one that seems to best reduce the noise in the energy and energy gradients.

"multiplicity"

The multiplicity of the system is listed after this keyword. For example, a doublet would require the line

$$multiplicity \quad 2$$

in the input deck. The default is a singlet state.

"charge"

The charge of the system is listed after this keyword. For example, a cation would require the line

$$charge \quad +1$$

in the input deck. The default is an uncharged system. Once the charge and multiplicity of the system have been defined, either explicitly or implicityly through the default values, the program will check to see if the two make sense for the system in question.

"maxiterations"

The maximum number of iterations in an SCF procedure is listed after this keyword. The default value is 40.

"maxgeometries"

The maximum number of steps in geometry optimization procedure is listed after this keyword. The default value is 10.

"mixing"

The mixing parameter for the SCF procedure is listed after this keyword. For example, if one wishes to mix 40% of the new density with 60% of the previous iteration's density, then one would have to include the following line

$$mixing \quad 0.40$$

in the input deck. The default value is 0.25.

"maxstep"

The maximum step size in a geometry optimization is defined after this keyword. The default value, 0.25, means that the average displacement of the atoms cannot exceed 0.25 atomic units in any one step of the geometry optimization.

"econvergence"

The convergence criterion for the SCF procedure is defined after this keyword. The default value is 0.000001. For an SCF procedure to be declared converged, the change in the total energy, in atomic units, and the maximum change in any one element of a density matrix, must be below the value defined after *"econvergence"*.

"gconvergence"

The convergence criterion for the geometry optimization is defined after this keyword. The default value is 0.001. For a geometry optimization to be declared converged, the maximum component of the gradient vector and the maximum change in any one nuclear coordinate must be below the value defined after *"gconvergence"* (in atomic units).

"hessian"

The procedure used for updating geometries in a geometry optimization run is defined after this keyword. If a value of 0 is listed after *"hessian"*, then the steepest descent approach is used. If a value of 1 is listed, then the conjugate gradient method is used. A value of 2, the default value, invokes the BFGS scheme in cartesian coordinates. A value of 3 invokes the BFGS scheme in internal coordinates. Finally, a value of 4 will invoke Baker's algorithm for locating transition states. In the latter two cases, 3 and 4, the geometry must be defined in internal coordinates rather than cartesian coordinates (both are acceptable for options 0, 1, and 2). If the value 4 is used to locate a transition state, then an initial estimate of the hessian must be supplied in the hessian file (unit 47) and it must yield one negative eigenvalue.

"diis"

Pulay's DIIS scheme (P. Pulay, *J. Comp. Chem.* **3**, 556 (1982)) for accelerating the convergence of the SCF procedure is either turned on or off by simply following the *"diis"* keyword with *"on"* or *"off"*. The default value is *"on"*.

"levelshift"

A non-zero value following this keyword will invoke Carbo's levelshifting scheme (R. Carbo, *Chem. Phys. Lett.* **47**, 581 (1977)). The value specified (in eV) after *"levelshift"* will lower occupied orbitals by that amount and raise virtual orbitals by the same amount. The default value is 0.0, i.e., Carbo's algorithm is not active. This can be used when convergence is complicated by a small HOMO/LUMO gap. This should be used when an SCF is restarted after an unsuccessful SCF. It is important to note that the orbital energies printed out at the end of the output file are indeed the unshifted orbital energies. If the Aufbau principle is followed, then the calculation worked properly. Otherwise, the highest lying occupied orbital should actually be emptied and the lowest lying virtual orbital should be reassigned that electron so as to get the true ground state of the system.

"initial-hessian"

The *"initial-hessian"* keyword is used to declare whether or not an initial guess at the geometry and hessian is available from a lower level of theory. If yes, then *"yes"* should be stated. If not,

then *"no"*. The default is *"no"*. An initial guess at the hessian must be made if one is trying to locate a transition state, and it must also contain one negative eigenvalue.

"point-charges"

This keyword is used when one wishes to create a reaction field by placing point charges around a molecule. The x, y, and z coordinates, as well as the actual charge of the particles, follow on subsequent lines, one line per point charge. As with the geometry specification, if the coordinates are in Angstroms, then the *"angstroms"* keyword should follow the *"point-charges"* keyword. Otherwise, the default is atomic units. Again, as in the geometry input, the list of point charges is terminated by a line that simply contains the keyword *"end"*.

"freeze"

When performing a geometry optimization in internal coordinates, i.e., 3 is listed after the *"hessian"* keyword, it is possible to freeze internal coordinates to the values listed in the z-matrix used to define the starting geometry. To do so, the keyword *"freeze"* is followed by appropriate integer values. The integer value assigned to each internal coordinate is its order of appearance in the z-matrix, going from left to right, line by line. For example, the first bond length is assigned a value of 1, the second, 2, the third, 4, the fourth, 7, the fifth, 10, and so on.

"end"

The *"end"* keyword is used to indicate that all the desired options have been invoked. This serves as the separation between the input options and the specification of the basis sets.

Specification of the Auxiliary and Orbital Basis Sets

The basis sets to be used are defined. First, atom by atom (skipping any dummy atoms which may be present), and one line per atom, the auxiliary basis sets are defined. The label must exactly match that found in the *bases* database which accompanies this program. Once the auxiliary basis sets are defined, the exact same procedure is repeated for the orbital basis sets. Please refer to the *methods* text, which accompanies the program, for an explanation of the labels used to distinguish the various orbital and auxiliary basis sets.