

Casimir program

The casimir program reads uncoupled local polarizabilities (i.e. of the form α_{tu}^{aa} , describing the response of multipole $t = jk$ on site a to an external field component $V_u = V_{j'k'}$ at the same site) for one or more molecules, recouples them (i.e. to the form $\alpha_{v(jj')}^{aa}$), and computes dispersion coefficients up to C_{12} . See below for details of the program organisation.

Data:

FREQUENCIES ω_0 n_{freq}

Specify the base frequency and the number of frequencies to be used for the quadrature, in a.u. No default.

SKIP [0 | 1]

By default, the static polarizability is not expected in the data file. If however it is present, SKIP or SKIP 1 will skip the first of each set of values, assuming it to be the static polarizability. SKIP 0 cancels a previous SKIP 1.

MOLECULE *name*

Subsequent polarizability data refers to the specified molecule.

SITE *name*

Introduces polarizability data for the site specified, in the current molecule. It comprises a number of sets of the form

$t \quad u$

$[\alpha(0)] \quad \alpha(\omega_1) \quad \alpha(\omega_2) \quad \dots \quad \alpha(\omega_n)$

terminated by “End” on a line by itself. Here t and u are spherical tensor indices (‘00’, ‘10’, ‘11c’, etc.). The polarizabilities, in a.u., follow on one or more lines. If the static polarizability is present, SKIP must be specified. (See above.)

PRINT {ALL | NONZERO}

Printing option for the recoupled polarizabilities. The default is to print only the nonzero ones.

CGDIR *path*

Specify the directory where the coupling coefficients are to be found, if not in the current directory. These are coupling coefficients for the real spherical tensor components.

RECOUPLE [ALL | *site site ...*]

Calculate recoupled polarizabilities for all sites, or for the sites specified. This is not needed if a DISPERSION command follows.

DISPERSION n A B

Recouple the polarizabilities for molecules A and B , if not already done, and calculate and print the dispersion coefficients between molecules A and B up to C_n . A and B may be the same. All coefficients up to C_n are calculated, but they will only be complete if all the contributing polarizabilities are provided. At present the program can handle polarizabilities up to quadrupole–hexadecapole and octopole–octopole. The results are printed in a form suitable for input into the Orient program, but note that many of the higher anisotropic terms are not implemented in Orient.

Programming notes

The dispersion coefficients are calculated from the localized polarizabilities using the procedure described in ?, §4.3.4. The localized polarizabilities are in the form α_{tu}^{aa} describing the response of multipole u on site a to field t at that site, or of multipole t to field u , where t and u are indices labelling spherical tensor components in the convention used by ?.

The first step is to recouple these (subroutine `recouple`):

$$\alpha_{JK}^{aa} = \sum_{tu} \alpha_{tu}^{aa} \langle tu|JK \rangle, \quad (1)$$

where $\langle tu|JK \rangle$ is a Clebsch–Gordan coefficient. However it is not a conventional Clebsch–Gordan coefficient $\langle j_1 m_1, j_2 m_2|JM \rangle$ that couples spherical tensors in complex form, but a modified version $\langle j_1 k_1, j_2 k_2|JK \rangle$ suitable for coupling two angular momenta or spherical tensors expressed in real components $t = j_1 k_1$ and $u = j_2 k_2$, into coupled components $|JK \rangle$, also in real form. These $\langle tu|JK \rangle$ coefficients have been evaluated using the `realcg` program in my RRF (root-rational-fraction) package. The directory `CamCASP/data/realcg` contains tables of these coupling coefficients: the file `realcg_p_q` contains tables for the angular momenta $j_1 = p$ and $j_2 = q$. Only the nonzero coefficients are listed. Each line of the file describes one nonzero coefficient in the form

$l_1 \ l_2 \ L \ i_1 \ i_2 \ i_3 \ i_4$

where l_1, l_2 and L are integers indexing the angular momentum components. l_1 and l_2 index the components of j_1 and j_2 respectively:

l_1 or l_2 : 0 1 2 3 4 5 6 ...

t or u : 0 1c 1s 2c 2s 3c 3s ...

while L indexes the coupled function JK as follows:

L: 0 1 2 3 4 5 6 7 8 9 ...

JK: 00 10 11c 11s 20 21c 21s 22c 22s 30 ...

The value of the coefficient is $(i_1/i_2) \sqrt{(i_3/i_4)}$. These coefficients may be pure imaginary, in which case $i_3 < 0$. $\sqrt{-n}$ always means $+i\sqrt{n}$. The transformation matrix between the uncoupled functions $|j_1 k_1, j_2 k_2 \rangle$ and the coupled functions $|JK \rangle$ is unitary.

The dispersion coefficients are now built, in subroutine `Cn`, from the usual integrals

$$\frac{\hbar}{2\pi(4\pi\epsilon_0)^2} \int_0^\infty \alpha_{L_A K_A(l_A' l_A)}^A(i\nu) \alpha_{L_B K_B(l_B' l_B)}^B(i\nu) d\nu, \quad (2)$$

which are evaluated, in function `cpint`, by Gauss–Legendre numerical quadrature. However these transform like product tensors $|L_A K_A \rangle |L_B K_B \rangle$, and have to be recoupled again using the `realcg` coefficients to obtain the dispersion coefficients in spherical-tensor form indexed by a single spherical-tensor label JK . The `realcg` coefficients have been evaluated once and for all, using the `C6coeffs` program in the RRF package, to give the explicit formulae which appear in the code files `c6code.f90`, `c7code.f90`, etc., which are included into subroutine `Cn`.

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References

Stone, A. J. (2013) *The Theory of Intermolecular Forces*, Oxford University Press, Oxford, 2nd edn.