

# CDA 2.2

## User's Guide

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## 1. Introduction

This is a short introduction to the usage of CDA. Part of theoretical background and applications are given in:

1. S. Dapprich, G. Frenking, *J. Phys. Chem.* **99**, 9352 (1995).
2. S. Dapprich, G. Frenking, *Angew. Chem. Int. Ed.* **34**, 354 (1995).
3. G. Frenking, S. Dapprich, A. W. Ehlers, S. F. Vyboishchikov, „*Stereoselective Reactions of Metal-Activated Molecules*“, Sonderforschungsbereich 347, Universität Würzburg, H. Werner and J. Sundermeyer (Eds), Vieweg, Braunschweig, 207 (1995).
4. G. Frenking, S. Dapprich, A. W. Ehlers, M. Otto, S. F. Vyboishchikov, „*Metal-Ligand Interactions: Structure and Reactivity*“, N. Russo and D. Salahub (Eds.), Proceedings of the NATO Advanced Study Institute, Cetraro (Italy), September 5 - 16, 1994, N. Russo (Ed.), p. 185 - 232, Kluwer Academic Publishers, Amsterdam (1996).

The charge decomposition analysis (CDA) has been devised to analyze chemical systems which can be described as donor-acceptor complexes. The electronic and energetic changes associated with the formation of a complex consisting of two fragments A and B are partitioned in terms of the familiar Dewar-Chatt-Duncanson model. The energy analysis is feasible within the Hartree-Fock approximation, while the charge decomposition analysis can also be carried out at correlated levels.

## 2. Theory

Although several outlines of the theoretical background have appeared already in the literature, some new aspects have not been published. In addition to the basic concepts, they are described in this chapter.

### 2.1. Charge Decomposition

The electron density  $\rho(\mathbf{r})$  of a closed-shell system can be written as

$$\rho(\mathbf{r}) = \sum_i m_i \phi_i^* \phi_i$$

where  $m_i$  are the occupation numbers of the canonical (or natural) molecular orbitals  $\phi_i$ . Expansion in an arbitrary basis  $\chi_\mu$  and integration leads to

$$q = \sum_i \sum_\mu \sum_\nu m_i c_{\mu i}^* c_{\nu i} \langle \chi_\mu | \chi_\nu \rangle$$

where  $q$  is the total number of electrons. Commonly the functions  $\chi_\mu$  are atomic orbitals. If one chooses a basis set constructed from fragment molecular orbitals (canonical or natural) derived from properly chosen fragments A and B, the summation can be decomposed into some significant parts. The entity

$$q_d = \sum_i \sum_\mu \sum_{v(<\mu)} 2m_i \left( \frac{m_\mu}{2} \right) \left( \frac{2-m_v}{2} \right) c_{\mu i}^* c_{v i} \langle \chi_\mu | \chi_v \rangle$$

can be termed as charge donation from fragment A to fragment B. In a similar manner, the electron donation in reverse direction (often called back donation) is then

$$q_b = \sum_i \sum_\mu \sum_{v(<\mu)} 2m_i \left( \frac{2-m_\mu}{2} \right) \left( \frac{m_v}{2} \right) c_{\mu i}^* c_{v i} \langle \chi_\mu | \chi_v \rangle$$

A third part, which describes the repulsive interactions between the fragment electrons and can therefore called repulsive polarization, is

$$q_r = \sum_i \sum_\mu \sum_{v(<\mu)} 2m_i \left( \frac{m_\mu}{2} \right) \left( \frac{m_v}{2} \right) c_{\mu i}^* c_{v i} \langle \chi_\mu | \chi_v \rangle.$$

## 2.2. Energy decomposition

CDA also partitions the Hartree-Fock energy  $E$  for a closed-shell system with  $n$  electrons. It is based on exactly the same transformations as the charge decomposition. The total energy can be written as

$$E = \sum_i \sum_\mu \sum_v^{n/2} c_{\mu i}^* c_{v i} \left( \langle \chi_\mu | \underline{F} | \chi_v \rangle + \langle \chi_\mu | \underline{H}^{\text{core}} | \chi_v \rangle \right) + V_{\text{NN}}$$

with  $\underline{F}$  being the Fock operator,  $\underline{H}^{\text{core}}$  being the core Hamilton operator and  $V_{\text{NN}}$  being the repulsion energy between all nuclei. Note that in the following expressions  $m_\mu$  and  $m_v$  have integral values and that the summation indices  $\mu$  and  $v$  run over all basis functions centered on A or B, respectively.

$$\begin{aligned} E_d &= \sum_i \sum_{\mu(A)} \sum_{v(B)}^{n/2} 2 \left( \frac{m_\mu}{2} \right) \left( \frac{2-m_v}{2} \right) c_{\mu i}^* c_{v i} \left( \langle \chi_\mu | \underline{F} | \chi_v \rangle + \langle \chi_\mu | \underline{H}^c | \chi_v \rangle \right) \\ E_b &= \sum_i \sum_{\mu(A)} \sum_{v(B)}^{n/2} 2 \left( \frac{2-m_\mu}{2} \right) \left( \frac{m_v}{2} \right) c_{\mu i}^* c_{v i} \left( \langle \chi_\mu | \underline{F} | \chi_v \rangle + \langle \chi_\mu | \underline{H}^c | \chi_v \rangle \right) \\ E_r &= \sum_i \sum_{\mu(A)} \sum_{v(B)}^{n/2} 2 \left( \frac{m_\mu}{2} \right) \left( \frac{m_v}{2} \right) c_{\mu i}^* c_{v i} \left( \langle \chi_\mu | \underline{F} | \chi_v \rangle + \langle \chi_\mu | \underline{H}^c | \chi_v \rangle \right) \end{aligned}$$

Omitting the summation over the index  $i$  leads to entities  $q_d(i)$ ,  $q_b(i)$ ,  $q_r(i)$ ,  $E_d(i)$ ,  $E_b(i)$ ,  $E_r(i)$ , which allow for the characterization of each specific MO of the complex. This is sometimes useful in investigating specific orbital interactions in a donor-acceptor complex.

### 2.3. Derived entities

The energy and charge components calculated by CDA can be used to define useful entities in order to gain more insight into the chemical bond of donor-acceptor complexes. For example, to define partial charges  $Q_A$  and  $Q_B$  for the fragments A and B, one could calculate

$$Q_A = q_d - q_b$$
$$Q_B = q_b - q_d = -Q_A$$

CDA also performs a Mulliken population analysis in the fragment orbital basis. The gross and net populations and the partial charges can be found in the output.

Additionally, the following characteristic entities  $\kappa$  which describe the „hardness“ of the specific electron reorganisation are calculated.

$$\kappa_d^{\text{CDA}} = \frac{E_d}{q_d} \quad \kappa_b^{\text{CDA}} = \frac{E_b}{q_b} \quad \kappa_r^{\text{CDA}} = \frac{E_r}{q_r}$$

## 3. Requirements

CDA2.2 is configured to work with the Gaussian03 and Gaussian09 program systems. It reads information about basis sets, wavefunctions, energies and occupation numbers from the three Gaussian output files:

### 3.1. The Molecule

The *first* file has to be a single point calculation of the complex. CDA reads in the molecular (canonical or natural) orbitals and the overlap matrix, both constructed in the AO space. The following keywords should be given additionally in the Gaussian keyword section:

<code>nosym</code>	(only necessary if the specified geometry is not in standard orientation)
<code>pop=full</code>	(print canonical orbitals; for a post Hartree-Fock analysis <code>pop=no</code> should be used)
<code>iop(3/33=1)</code>	(print one-electron integrals)
<code>iop(3/36=-1)</code>	(suppress computing of multipoles in L303)
<code>density</code>	(use the density matrix for the current method)

The geometry specification must be given in cartesian coordinates instead of a Z-matrix. The order in which the atoms appear is crucial and should not be changed in the fragment calculations (vide infra). Hence, a geometry specification of the complex is structured in the following manner:

```

0 1
donoratom1      x1  y1  z1
donoratom2      x2  y2  z2
donoratom3      x3  y3  z3
...
acceptoratom1   x4  y4  z4
acceptoratom2   x5  y5  z5
...

```

### 3.2. Fragment A

The *second* file is the output of a single point calculation of the fragment which is supposed to act as the electron donor. From this file CDA only needs the eigenvectors. The following keywords are necessary:

<code>nosym</code>	(prevent reorientation of the molecule)
<code>pop=full</code>	(print canonical orbitals; <code>pop=no</code> for post Hartree-Fock calculations)
<code>density</code>	(use the density matrix for the current method)

And the geometry specification:

```

0 1
donoratom1      x1  y1  z1
donoratom2      x2  y2  z2
donoratom3      x3  y3  z3
...

```

### 3.3. Fragment B

The *third* file is a single point calculation of the back donating fragment with exactly the same keywords as for the donor fragment. The geometry is specified as:

```

0 1
acceptoratom1   x4  y4  z4
acceptoratom2   x5  y5  z5
acceptoratom3   x6  y6  z6
...

```

## 4. Usage

CDA needs three command line arguments. The syntax is:

```
cda2.2 file1 file2 file3
```

with

<code>file1</code>	Gaussian output file of the complex calculation
<code>file2</code>	Gaussian output file of the donor fragment calculation
<code>file3</code>	Gaussian output file of the acceptor fragment calculation

The result of the analysis (mainly self-explanatory, hopefully) is printed through standard output. It can be redirected into a file using the special shell characters `>` or `>>`. For example:

```
cda2.2 bh3co.out co.out bh3.out > bh3co.cda
```

## 5. Appendix

CDA is written in pure ANSI-C. Therefore it should be possible to compile it on nearly every UNIX system. Go to the source folder of CDA2.2 and try

```
make
```

or refer to your local C-compiler manual (`man cc`) for further instructions.

The program uses dynamic memory allocation techniques for storage and transformation of integrals and matrices. The matrix inversion algorithm has been taken from: G. E. Forsythe, C. B. Moler, „*Computer Solutions of Linear Algebraic Systems*“, Chapter 18, Englewood Cliffs, N. J., **1967**, Prentice Hall.

At present stage only closed-shell fragments can be calculated. This is no serious disadvantage as in most cases they arise naturally. However, in certain transition metal compounds, the choice of appropriate donor and acceptor subsystems is somewhat arbitrary and could lead to peculiar results.

The program does not yet include complete error handling. Please ensure that the correct Gaussian files are provided.