

# Notes on calculation of molecular dipole moments and polarizabilities

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Molecular electronic properties are important in the study of intermolecular forces. It is possible (although not easy) to calculate dipole moment and polarizability from the microscopic definition, according to some textbook. If we only consider the electronic ground state ( $|0\rangle$ ):

$$\begin{aligned}\mu_\alpha &= \langle 0 | \hat{\mu}_\alpha | 0 \rangle \\ &= \int \rho_0(\mathbf{r}) r_\alpha d^3\mathbf{r},\end{aligned}\tag{1}$$

and

$$\alpha_{\alpha\beta} = \sum_{n \neq 0} \frac{\langle 0 | \hat{\mu}_\alpha | n \rangle \langle n | \hat{\mu}_\beta | 0 \rangle + \langle 0 | \hat{\mu}_\beta | n \rangle \langle n | \hat{\mu}_\alpha | 0 \rangle}{E_n - E_0},\tag{2}$$

where  $\alpha$  and  $\beta$  in subscripts may stand for  $x$ ,  $y$  or  $z$ . An example of calculating multipole moments can be found in MOLPRO User's manual:

```
***,h2o properties
geometry=
{o;h1,o,r;h2,o,r,h1,theta}    !Z-matrix geometry input
r=1 ang                        !bond length
theta=104                      !bond angle
gexpec,dm,sm,qm                !compute dipole and quarupole moments
$methods=[hf,multi,ci]         !do hf, casscf, mrci
do i=1,#methods                !loop over methods
  $methods(i)                  !run energy calculation
  e(i)=energy
  dip(i)=dmz                    !save dipole moment in variable dip
  quadxx(i)=qmxx                !save quadrupole momemts
  quady(i)=qmyy
```

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quadzz(i)=qmzz
smxx(i)=xx                !save second momemts
smyy(i)=yy
smzz(i)=zz
enddo
table,methods,dip,smxx,smyy,smzz
!print table of first and second moments
table,methods,e,quadxx,quady,quadzz
!print table of quadrupole moments

```

It is also possible to use finite electric field to get these properties since they are molecular electronic ones. Molecules in electric fields suffers from changes in energy, which is a function of both molecular properties and the extra electric fields. According to Rayleigh-Schrödinger Perturbation Theory and Taylor expansion, let us consider a uniform electric field, which is a vector. For simplicity, let it be  $\mathbf{V} = V \cdot \mathbf{x}$ . Energy of a molecule in such field should then be

$$\begin{aligned}
 E &= E^0 + E' + E'' \\
 &= \langle 0 | \hat{H}^0 | 0 \rangle + \mu_x \cdot V - \frac{1}{2} \alpha_{xx} V^2,
 \end{aligned}
 \tag{3}$$

from which the dipole moment is the first order derivative of energy to the external field and the polarizability the (negative) second order. In MOLPRO manual there is also an example:

```

***,H2O finite field calculations

r=1.85,theta=104          !set geometry parameters
geometry={0;              !z-matrix input
          H1,0,r;
          H2,0,r,H1,theta}
basis=avtz                !define default basis
field=[0,0.005,-0.005]    !define finite field strengths
$method=[hf,mp4,ccsd(t),casscf,mrci]

k=0
do i=1,#field              !loop over fields
  dip,,field(i)            !add finite field to H
  do m=1,#method           !loop over methods
    k=k+1
    $method(m)             !calculate energy
    e(k)=energy            !save energy
  enddo
enddo

k=0

```

```

n=#method
do m=1,#method
  k=k+1
  energ(m)=e(k)
  dipmz(m)=(e(k+n)-e(k+2*n))/(field(2)-field(3))
  !dipole moment as first energy derivative
  dpolz(m)=(e(k+n)+e(k+2*n)-2*e(k))
    /(((field(2)-field(1))*(field(3)-field(1))))
  !polarizability as second der.
enddo

table,method,energ,dipmz,dpolz
title,results for H2O, r=$R, theta=$theta, basis=$basis
---
```

Please find some more details in A. J. Stone's textbook<sup>1</sup>.

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<sup>1</sup>A. J. Stone, *The Theory of Intermolecular Forces*, Second Edition, Oxford University Press.