100626-1002

DL/SCI/TM18T

technical memorandum Daresbury Laboratory

DL/SCI/TM18T

CALCULATION OF PSEUDO-MOLECULAR ORBITALS FOR ELECTRON-MOLECULE COLLISIONS

by

J. KENDRICK, Daresbury Laboratory

DECEMBER, 1979

LENDING COPY.

Science Research Council

Daresbury Laboratory

Daresbury, Warrington WA4 4AD

Introduction

For the calculation of accurate electron-molecule collision processes, the molecular orbital basis must be flexible enough to describe the neutral molecule in its ground state, the neutral molecule perturbed by the electric field of the scattered electron and any relevant negative ion states in the energy region of interest. This necessarily leads to the use of large basis sets, causing computational problems in the scattering calculation. An approach adopted for atoms, involves generating the pseudo-states of the atoms and using these in a limited configuration interaction wavefunction. In the terms of perturbation theory the pseudo-states are the first order corrections to the unperturbed wavefunction. In this technical memorandum an alternative approach is given for molecules and a program based on this method is described.

Theory

Let us write the unperturbed target wavefunction Ψ^0 as a Slater determinant of molecular orbitals $\{\psi_i^0\}$. This restriction on the form of the wavefunction is not essential to the theory but aids its clarity. If a uniform field F, where F is a tensor, is applied to the molecule then the resulting wavefunction is:

$$\Psi(F) = \Psi^0 + \lambda\Psi^{(1)}(F) + \lambda^2\Psi^{(2)}(F) \text{ -----}$$

This may be simplified by considering only a single component of the field tensor and equating this with the perturbation parameter, λ.

$$\Psi = \Psi^0 + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} \text{ -----}$$

The other perturbed quantities of interest are the hamiltonian (H) and the energy (E).

$$H = H^0 - \lambda\hat{\mu}$$
$$E = E^0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \text{ -----}$$

where;

$$H^0\Psi^0 = E^0\Psi^0$$
$$H\psi = E\Psi$$

and $\hat{\mu}$ is a component of the dipole moment operator.

Perturbation theory gives;

$$E^{(1)} = -\langle\Psi^0|\hat{\mu}|\Psi^0\rangle$$

$$E^{(2)} = \sum_K \frac{\langle\Psi^0|\hat{\mu}|\Psi_K^0\rangle\langle\Psi_K^0|\hat{\mu}|\Psi^0\rangle}{(E^0 - E_K^0)} ,$$

and

$$\Psi^{(1)} = \sum_K \frac{\langle\Psi_K^0|\hat{\mu}|\Psi^0\rangle}{(E_K^0 - E^0)} \cdot \Psi_K^0$$

where Ψ_K^0 are excited states of the unperturbed molecule.

The following correspondences can be made;

$$-E^{(1)} = \mu, \text{ a component of the dipole moment}$$
$$2E^{(2)} = \alpha, \text{ a component of the polarisability}$$

For molecules without a dipole moment the polarisability is the most important quantity governing the reaction of the molecule to an applied field, and has shown to be important in the description of low energy electron scattering by atoms$^{(1)}$ and molecules$^{(2)}$. The generation of a pseudo-state, Ψ_P^0, may be seen in the following equation

$$\Psi^{(1)} = \frac{\langle\Psi_P^0|\hat{\mu}|\Psi^0\rangle}{(E_P^0 - E^0)} \cdot \Psi_P^0$$

where the sum over states expression for the first order perturbed wavefunction is replaced by a single term.

$\Psi(\lambda)$ may be represented by a single determinant of perturbed molecular orbitals, $\{\psi_i\}$. This is used by the finite-field method for the calculation of polarissbilities. However, in the scattering calculation it is convenient to use a single set of molecular orbitals, in most cases one chooses $\{\psi_i^0\}$.

The perturbed molecular orbitals can be written;

$$\psi_i = \psi_i^0 + \lambda \, \psi_i^{(1)} + \ldots\ldots$$

where $\psi_i^{(1)} = \sum_{k \neq i} C_{ki} \, \psi_i^0$

Substituting this into Ψ gives a configuration interaction expansion in terms of the unperturbed molecular orbitals. Thus within a normalisation factor;

$$\Psi = \Psi^0 + \sum_{ia} \left[\{C_{\bar{1}1}\} \, C_{ai} \, \Psi_i^a \right] + \text{double replacements}$$

$$+ \text{triple replacements}$$

Ψ_i^a means the occupied orbital ψ_i^0 in the determinant is Ψ^0 replaced by virtual ψ_a^0.

Atomic pseudo-state calculations$^{(3)}$ have truncated this expansion at the single replacement level and have determined the coefficients using a variation-perturbation method, which is equivalent to a finite-field calculation using the same configurations. Such calculations are not as reliable as finite-field calculations using perturbed Hartree-Fock wavefunctions due to the neglect of higher order replacements. So it is proposed that rather than calculate the single replacement configuration interaction wavefunction by a finite-field method, a suitable wavefunction can be calculated by projecting the perturbed Hartree-Fock wavefunction onto the unperturbed Hartree-Fock wavefunction and its single replacement configurations.

$$\sum_{ia} |\Psi_i^a\rangle \, \langle\Psi_i^a|\Psi\rangle = \sum_{ia} S_{ai} \, |\Psi_i^a\rangle$$

Apart from a normalisation factor, $C_{ai} = S_{ai}$, where;

$$S_{ai} = \langle\Psi_i^a|\Psi\rangle \quad .$$

An alternative derivation may be found by considering the maximisation of;

$$I = \langle\Psi| \, C_{00}\Psi^0 + \sum_{ia} C_{ia} \, \Psi_i^a \rangle$$

subject to the constraint that

$$N = \langle C_{00}\Psi^0 + \sum_{ia} C_{ai}\Psi_i \, | C_{00}\Psi^0 + \sum_{ia} C_{ai}\Psi_i \rangle = 1$$

Taking the derivative of $F = I + \lambda N$ (where λ is a lagrangian multiplier) with respect to C_{ai} gives;

$$S_{ai} + 2 \lambda \, C_{ai} = 0$$

$$C_{ai} = \frac{S_{ai}}{2\lambda}$$

where

$$\lambda = -\frac{1}{2} \left[\sum_{ia} S_{ai}^2 \right]^{1/2}$$

The virtual orbitals are able to mix amongst themselves without affecting the target wavefunction. This freedom can be used to improve the convergence of the single replacement expansion and so reduce the number of configurations required to represent the polarised molecule. Consider the orbital mixings induced by an applied field for diatomic molecules. Tables 1 and 2 give a summary of these interactions for homonuclear and heteronuclear diatomic molecules respectively.

Taking the model wavefunction in which a given occupied orbital is polarised by a single orbital of each symmetry and no polarising virtual orbital may be used to polarise more than one occupied orbital, then a new polarising, virtual orbital (a pseudo-orbital) can be written;

$$\psi_a^0 = \sum_b C_{bi} \, \psi_b^0 \quad ,$$

where the sum over b is a sum over all virtual orbitals belonging to the same symmetry as ψ_a^0, and where orbital ψ_i^0 is the occupied orbital which ψ_a^0 polarises. (Note that although a given occupied orbital may have many polarising orbitals a polarising orbital may polarise only one occupied orbital). The set of virtual orbitals generated in this way are no longer orthogonal. Orthogonality may be re-introduced by Schmidt orthogonalising the rest of the virtual orbitals to the polarising orbitals followed by symmetric orthogonalisation of all the virtual orbitals. This orthogonalisation mixes the virtual orbitals amongst themselves and it has been found necessary to repeat the process of projection, contraction and orthogonalisation 5 to 7 times before the second order property (the polarisability) becomes stable from iteration to iteration.

The model wavefunction described above is only suitable for defining the polarising, virtual orbitals. In practice such a wavefunction is not suitable for representing a polarised molecule. However, experience indicates that all single replacements from the occupied orbitals to the polarised pseudo orbitals provide a reasonable description of the polarised molecule. Finally it should be noted that the polarisability predicted by the wavefunction consisting of <u>all</u> single replacements is invariant to a unitary transformation in the virtual space.

Program Description

The program is compatible with the ATMOL3 package and takes the perturbed and unperturbed molecular orbitals from ATMOL3 dump files. Similarly, the final molecular orbitals may be stored on ATMOL3 files ready for use in further calculations. After reading into core the perturbed and unperturbed molecular orbital coefficients, the unperturbed molecular orbitals are divided into symmetry classes, which are then printed out. Then the overlap matrix,

$O_{ij} = \langle\psi_i|\psi_j^0\rangle$ is calculated, followed by;

$$S_{ai} = \langle\Psi|\Psi_i^a\rangle$$

$$= \begin{vmatrix} O_{11} & O_{12} & --- & O_{1N} \\ O_{21} & O_{22} & --- & O_{2N} \\ \vdots & \vdots & & \vdots \\ O_{N1} & O_{N2} & --- & O_{NN} \end{vmatrix} \cdot \begin{vmatrix} O_{11} & --- & O_{1i-1} & O_{1a} & O_{1i+1} & --- & O_{1N} \\ O_{21} & & ---- & O_{2a} & ---- & & O_{2N} \\ \vdots & & & \vdots & & & \vdots \\ O_{N1} & & ---- & O_{Na} & ---- & & O_{NN} \end{vmatrix}$$

The determinants being evaluated using the NAG library routine F03AAF.

From the configuration interaction coefficients C_{ai}, the polarisability is calculated for three types of wavefunction;

Scheme A	All single replacements
Scheme B	Single replacements of occupied orbitals to all polarising orbitals
Scheme C	Single replacements of occupied orbitals to their corresponding polarising orbitals only

Finally the virtual orbitals are rotated as described in the previous section, and the processes are iterated. Generally speaking there is no convergence as such. However after 5-7 iterations it is normally found that the polarisabilities for scheme B and C wavefunctions are quite stable and iteration can stop. The molecular orbitals produced in this way are not unique and different starting orbitals will produce different final orbitals.

Data Description

Data format follows the conventions used by the ATMOL3 system, that is free format input of alphanumeric characters, integer or real numbers.

Card 1 NBASIS NOCC NMAX FIELD NFIRST NITER IPRINT

NBASIS - number of basis functions

NOCC - number of doubly occupied orbitals

NMAX - highest orbitals to be used in the calculation
NMAX ≤ NBASIS

FIELD - field strength applied when generating the perturbed orbitals. If a field has been applied in 2 or 3 directions simultaneously it is assumed that the field strength is the same in all directions

NFIRST - The NFIRST to NOCC orbitals are to be used to generate single replacements
If NFIRST is not given NFIRST=1

NITER - The number of iterations required
If NITER is not given NITER=6

IPRINT =0 Then only the configuration interaction coefficients are printed out for every other iteration

=1 Overlap matrix and vectors are printed out in addition to above.

Note that if IPRINT=1 is required then NITER and NFIRST cannot be omitted as IPRINT=0 is default.

Next follow NOCC-NFIRST+1 cards of the type;

```
JPOL      KPOL(1)     KPOL(2)
```

JPOL - the occupied orbital being polarised

KPOL(I) - the KPOL(I)th virtual orbital polarises occupied orbital JPOL. Note that the first virtual orbital is KPOL(I)=1.

JPOL alone may be specified on this card, in which case no contributions will come from this orbital to scheme A configuration interaction wavefunctions but contributions will occur from schemes B and C. If these cards are left blank the program attempts one iteration and the configuration interaction wavefunction may be used to help assign the polarising orbitals.

Next follow three cards with the format;

```
EDX       IBLKX       ISECX
```

These cards specify the disposition of, respectively: the unperturbed molecular orbitals, the perturbed molecular orbitals and the contracted molecular orbitals on ATMOL3 data sets.

EDX - is the ATMOL3 data set name

IBLKX - is the starting block of the required dump file

ISECX - is the section containing the required molecular orbitals.

Files (on userid QCK)

The following refers to files relevant to the program available on the IBM 370/165 at Daresbury.

PROJECT.FORT	FORTRAN source
LOAD (PROJECT)	Load module
CNTL (PROJECT)	Compilation, linkage and storage of the program

EXAMPLE:

```
//       EXEC FGG,LIBRARY='QCK.LOAD', MEMBER=PROJECT
//G.ED1   DD  DSN=QCK.JKADUMP,DISP=SHR
//G.ED2   DD  DSN=QCK.JKBDUMP,DISP=SHR
//G.SYSIN DD  *
     38   7  38   0.004  5
     5       4  5 6
     6       1 10 11  2  3
     7       1 10 11  2  3
    ED1   1  1
    ED2  101 1
    ED1   1  2
/*
//
```

This is an example taken from a 38 basis function, Slater orbital calculation for N_2

The symmetry of the orbitals is as follows;

Occupied		Virtual	
5	σ_g	1	σ_g
6 7	π_u	2 3	π_g
		4	σ_u
		5 6	π_u
		10 11	δ_g

The degeneracy of the occupied π_u orbital leads to the duplication of the polarisers used for both components of the π_u orbital. The degeneracy of the contracted π_u orbital can be maintained by applying the same strength fields in the x and y directions simultaneously.

References

1. P.G. Burke, D.F. Gallaher and S. Geltmann, J. Phys. B2, (1969) 1142.

2. F.H. Faisal and A. Temkin, Phys. Rev. Lett. 28, (1972) 203.

3. P.G. Burke and J.F.B. Mitchell, J. Phys. B7, (1974) 665.

TABLE 1

Orbital Mixings Induced by an Applied Field

Homonuclear Diatomic Molecule

The Applied Field Induces Mixing with Orbitals of the Following Symmetry

Orbital	Perpendicular Field	Parallel Field
σ_g	π_u	σ_u
σ_u	π_g	σ_g
π_g	δ_u, σ_u	π_u
π_u	δ_g, σ_g	π_g
δ_g	ϕ_u, π_u	δ_u
δ_u	ϕ_g, π_g	δ_g

TABLE 2

Orbital Mixings Induced by an Applied Field

Heteronuclear Diatomic Molecule

The Applied Field Induces Mixing with Orbitals of the Following Symmetry

Orbital	Perpendicular Field	Parallel Field
σ	π	σ
π	δ, σ	π
δ	ϕ, π	δ

NINA 43