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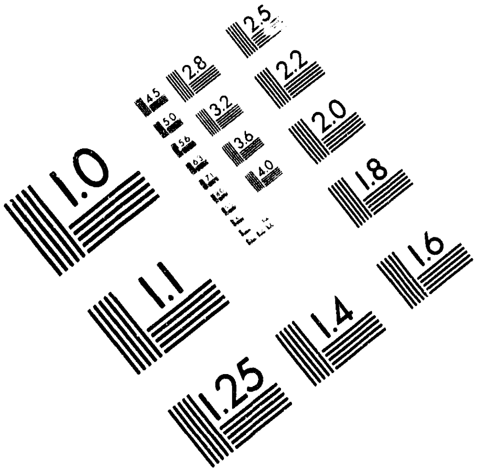

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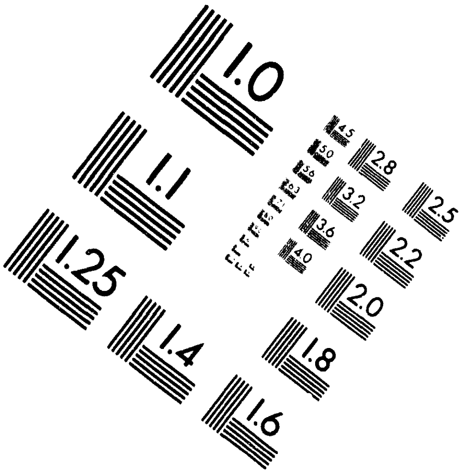

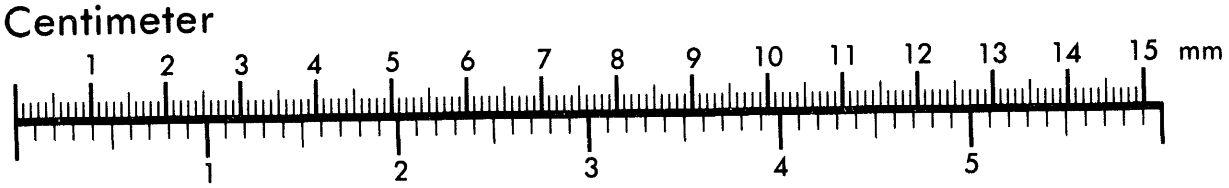

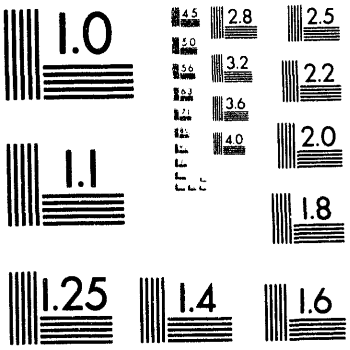

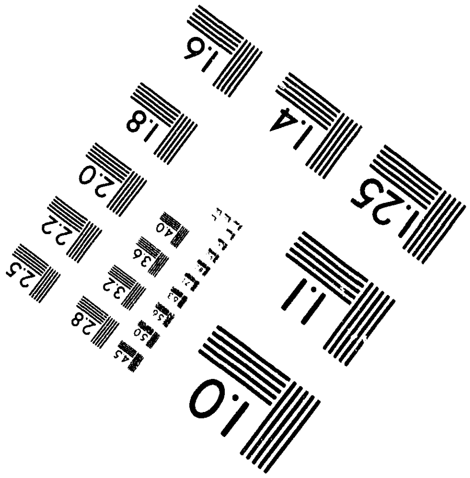

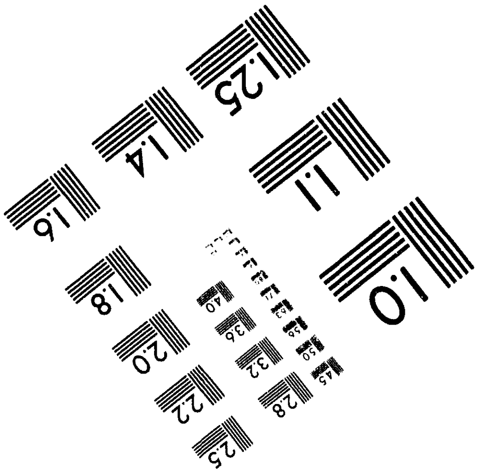

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MCHF calculations of isotope shifts;
I Program implementation and test runs
II Large-scale active space calculations

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Abstract

A new isotope shift program, part of the MCHF atomic structure package, has been written and tested. The program calculates the isotope shift of an atomic level from MCHF or CI wave functions. The program is specially designed to be used with very large CI expansions, for which angular data cannot be stored on disk. To explore the capacity of the program, large-scale isotope shift calculations have been performed for a number of low lying levels in *B I* and *B II*. From the isotope shifts of these levels the transition isotope shift have been calculated for the resonance transitions in *B I* and *B II*. The calculated transition isotope shifts in *B I* are in very good agreement with experimental shifts, and compare favourably with shifts obtained from a many-body perturbation calculation.

Part I

Isotope shift, program implementation and test runs

1 Introduction

The isotope shifts observed in atomic transitions arise from the finite nuclear mass and size. Conventionally the isotope shift is expressed as a sum of the mass and field shift. ¿From a physical point of view the field shift is the more interesting, since it yields information about the nuclear charge distribution. One of the goals of *ab initio* calculations is to determine the mass shift as to enable the field shift to be extracted from the experimentally observed isotope shift. Unfortunately, it has shown exceedingly difficult to calculate the mass shift accurately. In order to obtain reliable results very large configuration expansions have to be used, where quadruple excitations are included.

The purpose of this study is to explore the capacity of a new isotope shift program, designed to be used with very large configuration interaction (CI) expansions.

2 Theory

The starting point for non-relativistic atomic calculations is the zero-order Hamiltonian (in a.u.)[1]

$$H_0 = \sum_{i=1}^{N}\left(-\frac{\nabla_i^2}{2m} - \frac{Z}{r_i}\right) + \sum_{i<j}^{N}\frac{1}{r_{ij}} \tag{1}$$

where the nucleus is assumed to be a point charge of infinite mass. In accurate calculations effects arising from the finite nuclear mass and size must be taken into account. This is normally done by treating these effects as perturbations.

2.1 Mass shift

For a finite nuclear mass, M, the kinetic energy of the nucleus must be considered. Using the momentum conservation law in the center of mass coordinate system, the operator for the internal kinetic energy of an N-electron atom becomes [1]

$$H_{kin} = -\sum_{i=1}^{N}\frac{\nabla_i^2}{2\mu} - \frac{1}{M}\sum_{i<j}^{N}\nabla_i \cdot \nabla_j . \tag{2}$$

The first term includes a correction to the electron mass in which the mass m is replaced by the reduced mass, $\mu = Mm/(M+m)$. This correction to the electron mass can be accounted for by multiplying the energy levels E_0, calculated from the zero-order Hamiltonian, with $M/(M+m)$. The resulting energy correction to the level E_0 is then given by

$$E_{nms} = -E_0\frac{m}{M+m} \tag{3}$$

---

[1] In atomic units $m = 1$, but it is included explicitly to avoid missunderstandings.

This is the normal mass shift (nms). The inclusion of the second term leads to an additional energy correction known as the specific mass shift (sms).

$$E_{sms} = -\langle\psi|\frac{1}{M}\sum_{i<j}^{N}\nabla_i \cdot \nabla_j|\psi\rangle \tag{4}$$

As first noted by Stone [2] the specific mass shift operator can be put into a more familiar tensorial form.

$$H_{sms} = -\frac{1}{M}\sum_{i<j}^{N}\nabla_i \cdot \nabla_j = -\frac{1}{M}\sum_{i<j}^{N}\nabla_i^{(1)} \cdot \nabla_j^{(1)} \tag{5}$$

where

$$\nabla^{(1)} = \mathbf{C}^{(1)}\frac{\partial}{\partial r} - \frac{\sqrt{2}}{r}(\mathbf{C}^{(1)}\mathbf{l})^{(1)} \tag{6}$$

Using the relation

$$\langle l||(\mathbf{C}^{(1)}\mathbf{l})^{(1)}||l'\rangle = \frac{l(l+1) - 2 - l'(l'+1)}{2\sqrt{2}}\langle l||\mathbf{C}^{(1)}||l'\rangle \tag{7}$$

it is seen that the gradient operator can be factorized in a radial and an angular part

$$\nabla^{(1)} = \nabla_r \mathbf{C}^{(1)} \tag{8}$$

where the radial part is given by

$$\nabla_r = \frac{\partial}{\partial r} - \frac{l(l+1) - 2 - l'(l'+1)}{2r} \tag{9}$$

Finally, substituting this into eq.(5) we get the tensorial form of the specific mass shift operator

$$H_{sms} = -\frac{1}{M}\sum_{i<j}^{N}\nabla_{r_i}\nabla_{r_j}(\mathbf{C}_i^{(1)} \cdot \mathbf{C}_j^{(1)}) \tag{10}$$

This tensorial form is the same as that for the $k = 1$ term in the expression for the electrostatic interaction between the electrons

$$\sum_{i<j}^{N}\frac{1}{r_{ij}} = \sum_{i<j}^{N}\sum_{k}\frac{r_<^k}{r_>^{k+1}}(\mathbf{C}_i^{(k)} \cdot \mathbf{C}_j^{(k)}) \tag{11}$$

Thus, the computational apparatus set up for the calculation of the electrostatic interaction matrix elements can, with small modifications, be used also for the specific mass shift.

2.2 Field shift

Due to the finite size of the nucleus the potential inside the nuclear charge distribution deviates from the potential of a point charge Z. For light atoms, where non-relativistic wavefunctions can be used, the resulting energy correction to the level E_0 is given by

$$E_{fs} = \frac{2\pi}{3}Z\langle r_N^2\rangle|\psi(0)|^2 \tag{12}$$

where $\langle r_N^2 \rangle$ is the mean square radius of the nucleus. Using the Dirac delta function the field shift (fs) can be written

$$E_{fs} = \frac{2\pi}{3} Z \langle r_N^2 \rangle |\psi(0)|^2 = \frac{2\pi}{3} Z \langle r_N^2 \rangle \langle \psi | \sum_{i=1}^{N} \delta(\mathbf{r}_i) | \psi \rangle \tag{13}$$

Noting that $4\pi r^2 \delta(\mathbf{r}) = \delta(r)$ we can write the field shift operator in tensorial form

$$H_{fs} = \frac{1}{6} Z \langle r_N^2 \rangle \sum_{i=1}^{N} \delta(r_i) r_i^{-2} \tag{14}$$

3 Program implementation

The present isotope shift program, part of the muliticonfiguration Hartree-Fock (MCHF) atomic structure package [3], is a complement to the old isotope shift program [4] that requires access to the angular files produced by the MCHF_NONH or MCHF_BREIT programs [5, 6]. The new program calculates the isotope shift without any reference to files containing angular information and can therefore be used with very large CI expansions.

3.1 Outline of method

In the multi-configuration Hartree-Fock method the atomic state wavefunction, ψ, is expanded in terms of configuration-state functions (CSFs) with the same LS term

$$\psi = \sum_{i=1}^{m} c_i \Phi(\gamma_i LS) \tag{15}$$

The configuration-state functions, $\Phi(\gamma_i LS)$, are antisymmetrized eigenfunctions to L^2, L_z, S^2, S_z and parity, which can be written as sums of products of spin-orbitals

$$\phi(r, \theta, \varphi, \sigma) = \frac{1}{r} P_{nl}(r) Y_{lm_l}(\theta, \varphi) \xi_{m_s}(\sigma) \tag{16}$$

where $Y_{lm_l}(\theta, \varphi)$ is a spherical harmonic and $\xi_{m_s}(\sigma)$ a spin function. By demanding the energy functional, $\langle \psi | H_0 | \psi \rangle$, for the atomic state wavefunction to be stationary with respect to variations in the radial functions and expansion coefficients, a system of coupled non-linear differential equations, one for each function, together with an eigenvalue problem for the expansion coefficients, is obtained. This problem is then solved by the self-consistent field (SCF) method [7, 8].

When a set of radial functions $P_{nl}(r)$ has been obtained from an MCHF calculation, the atomic state wavefunction can be expanded in CSFs where now only the expansion coefficients have to be determined. This is done by diagonalizing the Hamiltonian matrix. Using a sparse matrix representation large expansions can be used. On a modern workstation expansions with more than 60 000 CSFs can be handled, the limit usually set by the available diskspace. CI techniques also exsist in which the explicit storage of the Hamiltonian matrix is avoided, and the eigenvectors obtained iteratively using Newton-Raphson type algorithms. For these techniques only the Hamiltonian matrix times a vector has to be stored, and therefore extremely large CI expansions can be used [9].

3.2 Calculation of the specific mass shift

Using standard Racah algebra techniques the evaluation of the specific masss shift from CSF expansions can be reduced to a summation over radial two-particle matrix elements.

$$\langle\psi|H_{sms}|\psi\rangle = \sum_{i,i'} c_i c_{i'} \langle\gamma_i LS|H_{sms}|\gamma_{i'} LS\rangle \tag{17}$$

After the angular integrations have been performed, the matrix element between two configuration states may be expressed as

$$\langle\gamma_i LS|H_{sms}|\gamma_{i'} LS\rangle = \sum_{nl} \text{Coeff}(1, n_1l_1, n_2l_2; n_3l_3, n_4l_4)_{ii'} \langle n_1l_1||\nabla_r||n_3l_3\rangle\langle n_2l_2||\nabla_r||n_4l_4\rangle \tag{18}$$

where the sum on nl is over all ordered sets of four orbital indices, $n_1l_1, n_2l_2; n_3l_3, n_4l_4$, the first two from γ_i and the other two from $\gamma_{i'}$. The coefficient Coeff$(1, n_1l_1, n_2l_2; n_3l_3, n_4l_4)_{ii'}$, the same as the coefficient for the Slater integral $R^1(n_1l_1, n_2l_2; n_3l_3, n_4l_4)$ in the expression for the electrostatic interaction between these two configuration states, is non-zero only if $l_1 = l_3 \pm 1$ and $l_2 = l_4 \pm 1$

The radial matrix element of the gradient operator between one-electron orbitals is given by the expression

$$\langle nl||\nabla_r||n'l'\rangle = \int_0^\infty P_{nl}(r)\left(\frac{d}{dr} - \frac{l(l+1) - l'(l'+1)}{2r}\right)P_{n'l'}(r)dr \tag{19}$$

3.3 Calculation of the field shift

In the same way the evaluation of the field shift operator from CSF expansions can be reduced to a summation over radial one-particle matrix elements.

$$\langle\psi|H_{fs}|\psi\rangle = \sum_{i,i'} c_i c_{i'} \langle\gamma_i LS|H_{fs}|\gamma_{i'} LS\rangle \tag{20}$$

Since the field shift operator is a tensor operator of rank zero, the matrix element between two configuration states may be expressed as

$$\langle\gamma_i LS|H_{fs}|\gamma_{i'} LS\rangle = \lambda \sum_{nl} \text{Coeff}(1, n_1l_1; n_2l_2)_{ii'} \langle n_1l_1||\delta(r)r^{-2}||n_2l_2\rangle \tag{21}$$

where the sum on nl is over all ordered sets of two orbital indices, $n_1l_1; n_2l_2$, the first one from γ_i and the other one from $\gamma_{i'}$. λ is a constant that contains the nuclear data and the coefficient $Coeff(1, n_1l_1; n_2l_2)_{ii'}$ is determined by standard Racah algebra techniques [10] and is nonzero only if $l_1 = l_2$.

The radial matrix element of the field shift operator between one-electron orbitals is given by the expression

$$\langle nl||\delta(r)r^{-2}||n'l'\rangle = \delta_{l,0}\delta_{l',0} AZ(nl) AZ(n'l') \tag{22}$$

where $AZ(nl)$ is the radial starting parameter

$$AZ(nl) = \left(\frac{P_{nl}(r)}{r^{l+1}}\right)_{r\to 0} \tag{23}$$

3.4 Program structure

Since the structure of the specific mass shift and field shift operators is very different, the former beeing a two-particle operator and the latter a one-particle operator, the calculation of the shifts is done by two different computer programs.

3.5 Specific mass shift program

This program calculates the specific mass shift parameter

$$S = -\langle\psi|\sum_{i<j}^{N} \nabla_i \cdot \nabla_j |\psi\rangle \tag{24}$$

from wich the specific mass shift of a specific isotope with nuclear mass M is obtained by a scaling with $1/M$. The program is to a large extent based on the MCHF_NONH program for computing integrals of the non-relativistic Hamiltonian [5]. To run the program a number of input files have to be supplied. If the wavefunction has been obtained from an MCHF calculation the < *name* >.c and < *name* >.g files are read. The < *name* >.c file contains the configurations, their couplings and the weights. The < *name* >.g file contains the radial integrals (19). If, instead, the wavefunction has be obtained from a CI calculation the configuration weights are read from < *name* >.l. The < *name* >.g file must in this case be taken from the MCHF calculation that generated the orbital basis used in the CI calculation. The program operation can be summarized as follows;

- The configuration weights are read.
- The radial integrals are read and sorted according to the orbital ordering defined by the configuration list
- The program loops over the left- and right-hand configuration states and the weights c_i and $c_{i'}$ are multiplied with the corresponding radial matrix elements and angular coefficients to give the contribution from the i, i' configuration pair. The contributions from each configuration pair are summed up to give the total value of the specific mass shift parameter.

Since the specific mass shift program only needs to evaluate the coefficients of the $k = 1$ term in the expression for the electrostatic interaction (11), the computation time can be cut down compared with the evaluation of the coefficients of all terms as done in MCHF_NONH. To restrict the evaluation to the $k = 1$ term changes have been made in the subroutine fano.

3.6 Field shift program

The expectation value of the field shift operator, a one-particle tensor operator of rank zero, is most easily computed within the framework of the previous hyperfine structure (hfs) program [11] based on Robbs program to evaluate reduced matrix elements of summations of one-particle tensor operators [10]. The calculation of the electron density at the nucleus $|\psi(0)|^2$ has been added as an option to the hfs program and from this quantity the field shift is easily obtained by multiplying with $\frac{2\pi}{3}Z\langle r_N^2\rangle$. The general structure of the program as well as the input files needed to run the program has been described in the original write-up of the hfs program [11].

4 Transition isotope shift

The observable effect of the isotope shift is a change of the transition energy between an upper and a lower atomic state. Different isotopes of a given element will have different transition energies. The measured difference in transition energy for two isotopes can directly be compared with the calculated difference.

4.1 Support program

Given the total non-relativistic energies E_0, the specific mass shift parameters S and the electron densities $|\psi(0)|^2$ for the upper and lower atomic states as well as the nuclear masses M and mean square radii $\langle r_N^2 \rangle$ for the isotopes, the transition energies of the isotopes can be calculated. These calculations are basically simple but involves a number of unit conversions. In order to minimize blunders a small support program has been written that calculates the transition energies from the parameters above. The program asks for the following data:

- specification of the transition
- zero order energy E_0 for the lower and upper state
- specific mass shift parameter S for the lower and upper state
- electron density at the nucleus $|\psi(0)|^2$ for the upper and lower state
- number of isotopes
- isotope labels
- isotope masses M
- root mean square nuclear radii $\langle r_N^2 \rangle^{1/2}$ of the isotopes
- number of electrons in the atom or ion

4.2 Examples

The Test Run output contains calculations of the specific mass shift parameter and the electron density for the $1s^2 2s^2\ {}^1S$ and $1s^2 2s2p\ {}^1P$ states in *B II*. The configuration expansions have been obtained by single, double, triple and quadruple excitations to the $3s2p1d$ active set of orbitals. The initial wavefunctions have been obtained from earlier runs. From the parameters obtained for these two states the transition energies are calculated for the isotopes with masses 10 and 11 u.

TEST RUN OUTPUT

```
                                      =======> Case 1 1s(2)2s(2) 1S.

>> lsgen                              =======> Obtain configuration list
 New list, add to existing list, expand existing list, optimized sorting,
 restored order or quit? (*/a/e/s/r/q)
>
 Breit or MCHF? (B/*)
>
 Default, symmetry or user specified ordering? (*/s/u)
>
 Highest principal quantum number, n? (1..15)
>3
 Highest orbital angular momentum, l? (s..d)
>d
 Are all these nl-subshells active? (n/*)
>
 Limitations on population of n-subshells? (y/*)
>
 Highest n-number in reference configuration? (1..3)
>2
 Number of electrons in 1s? (0..2)
>2
 Number of electrons in 2s? (0..2)
>2
 Number of electrons in 2p? (0..6)
>0
 Resulting term? (1S, 3P, etc.)
>1S
 Number of excitations = ? (0..4)
>4
 63 configuration states have been generated.
 Generate a second list? (y/*)
>
 63 configuration states in the final list.
 The generated file is called clist.out.



>> mv clist.out clist                 =======> Move clist.out clist

>> ynonh                              =======> Obtain energy expression
  NEW(ALL=0), N-ZERO(ALL=0)
>0,0



>> yspmchfiso                         =======> Obtain radial functions and integrals
 ATOM, TERM, Z in FORMAT(A,A,F) :
>BII,1S,5.
  Enter the number of the eigenvalue
>1
```

```
 There are   6 orbitals as follows:
   1s  2s  2p  3s  3p  3d
 Enter orbitals to be varied: (ALL,NONE,SOME,NIT=,comma delimited list)
>all
 Default electron parameters ? (Y/N)
>y
 Default values for other parameters ? (Y/N)
>y


>> mv cfg.out 3s2p1d1S.c                        =======> Move cfg.out to 3s2p1d1S.c
>> mv wfn.out 3s2p1d1S.w                        =======> Move wfn.out to 3s2p1d1S.w
>> mv gradint 3s2p1d1S.g                        =======> Move gradint (contains the radial
                                                          integrals needed to calculate the
                                                          specific mass shift) to 3s2p1d1S.g



>> yisonew                                      =======> Calculation of the specific mass
                                                          shift parameter
  Name of state
>3s2p1d1S
  Input from an MCHF (M) or CI (C) calculation ?
>m



>> cat 3s2p1d1S.i                               =======> Display the 3s2p1d1S.i file

   ================================
    Specific mass shift parameter S
   ================================

   Contributions to the parameter
   from G and R integrals (in a.u.)

  -7.994567157962930 2E-02    G integrals
   0.7051286994066368         R integrals

   Total value of S (in a.u.)

   0.6251830278270075

   Total value of S (in cm-1)

    68605.90706986833



>> hfsdens                                      =======> Calculation of the electron density
  Name of state
>3s2p1d1S
```

```
                    Hyperfine structure and electron density calculation

 Electron density at the nucleus ? (Y/N)
>y
 Hyperfine structure calculation ? (Y/N)
>n
 Input from an MCHF (M) or CI (C) calculation ?
>m
  Contributions from different configuration
  subspaces (Y/N)
>n


>> cat 3s2p1d1S.h                     =======> Display the 3s2p1d1S.h file

  ==============================
   Electron density calculation
  ==============================


  Electron density at the nucleus (a.u.^-3)


  J     J

  0     0       72.49048445

                                      =======> Case 2 1s(2)2s(1)2p(1) 1P.

>> lsgen                              =======> Obtain configuration list
 New list, add to existing list, expand existing list, optimized sorting,
 restored order or quit? (*/a/e/s/r/q)
>
 Breit or MCHF? (B/*)
>
 Default, symmetry or user specified ordering? (*/s/u)
>
 Highest principal quantum number, n? (1..15)
>3
 Highest orbital angular momentum, l? (s..d)
>d
 Are all these nl-subshells active? (n/*)
>
 Limitations on population of n-subshells? (y/*)
>
 Highest n-number in reference configuration? (1..3)
>2
 Number of electrons in 1s? (0..2)
>2
 Number of electrons in 2s? (0..2)
>1
 Number of electrons in 2p? (0..6)
>1
 Resulting term? (1S, 3P, etc.)
```

```
>1P
 Number of excitations = ? (0..4)
>4
 98 configuration states have been generated.
 Generate a second list? (y/*)
>
 98 configuration states in the final list.
 The generated file is called clist.out.



>> mv clist.out clist                          =======> Move clist.out clist

>> ynonh                                       =======> Obtain energy expression
  NEW(ALL=0), N-ZERO(ALL=0)
>0,0



>> yspmchfiso                                  =======> Obtain radial functions and integrals
 ATOM, TERM, Z in FORMAT(A,A,F) :
>BII,1P,5.
  Enter the number of the eigenvalue
>1

 There are   6 orbitals as follows:
   1s  2s  2p  3s  3p  3d
 Enter orbitals to be varied: (ALL,NONE,SOME,NIT=,comma delimited list)
>all
 Default electron parameters ? (Y/N)
>y
 Default values for other parameters ? (Y/N)
>y


>> mv cfg.out 3s2p1d1P.c                       =======> Move cfg.out to 3s2p1d1P.c
>> mv wfn.out 3s2p1d1P.w                       =======> Move wfn.out to 3s2p1d1P.w
>> mv gradint 3s2p1d1P.g                       =======> Move gradint (contains the radial
                                                        integrals needed to calculate the
                                                        specific mass shift) to 3s2p1d1P.g



>> yisonew                                     =======> Calculation of the specific mass
                                                        shift parameter

 Name of state
>3s2p1d1P
 Input from an MCHF (M) or CI (C) calculation ?
>m



>> cat 3s2p1d1P.i                              =======> Display the 3s2p1d1P.i file
```

```
  =================================
   Specific mass shift parameter S
  =================================

  Contributions to the parameter
  from G and R integrals (in a.u.)

 -0.4426032127994707        G integrals
  0.7340438759260572        R integrals

  Total value of S (in a.u.)

  0.2914406631265865

  Total value of S (in cm-1)

   31981.91595242094


>> hfsdens                                 =======> Calculation of the electron density
 Name of state
>3s2p1d1P

                      Hyperfine structure and electron density calculation

 Electron density at the nucleus ? (Y/N)
>y
 Hyperfine structure calculation ? (Y/N)
>n
 Input from an MCHF (M) or CI (C) calculation ?
>m
  Contributions from different configuration
  subspaces (Y/N)
>n


>> cat 3s2p1d1P.h                          =======> Display the 3s2p1d1P.h file

  ==============================
   Electron density calculation
  ==============================


  Electron density at the nucleus (a.u.^-3)


  J     J

  1     1       70.69252181


                                          =======> Case 3 transition isotope shift

>>isosupport
```

```
 Specify the transition
>1s(2)2s(2) 1S - 1s(2)2s(1)2p(1) 1P in BII
 Nuclear charge
>5.
 Energy (a.u.) infinite nucl. mass for lower state
>-24.296413
 Energy (a.u.) infinite nucl. mass for upper state (1) or
 energy diff. (cm^-1) between upper and lower state (2)
>1
 Energy (a.u.) infinite nucl. mass for upper state
>-23.988668
 Value of sms parameter S (a.u.) for lower state
>0.62518
 Value of sms parameter S (a.u.) for upper state
>0.29144
 Electron density (a.u.^-3) at the nucleus for lower state
>72.490
 Electron density (a.u.^-3) at the nucleus for upper state
>70.692
 Number of isotopes
>2
 Isotope label (character*4)
> 10B
 Isotope mass (u)
>10.012937
 Root mean square nuclear radius sqrt(<r**2 >) (fm)
>2.44
 Isotope label (character*4)
> 11B
 Isotope mass (u)
>11.009305
 Root means quare nuclear radius sqrt(<r**2 >) (fm)
>2.38
 Number of electrons
>4


>>cat isodata                              =======> Display isodata file containing
                                                    information about the isotope shift

 ==============
  Initial data
 ==============

  Transition
  1s(2)2s(2) 1S - 1s(2)2s(1)2p(1) 1P in BII

  Nuclear charge   5.000000000000000

  Energy (a.u.) infinite nucl. mass for lower state  -24.29641300000000    H
  Energy for upper state from calculation
  Energy (a.u.) infinite nucl. mass for upper state  -23.98866800000000    H

  Value of sms parameter S (a.u.) for lower state  0.6251800000000000    H
```

```
Value of sms parameter S (a.u.) for upper state  0.2914400000000000    H

Electron density (a.u.^-3) at the nucleus for lower state   72.49000000000000
Electron density (a.u.^-3) at the nucleus for upper state   70.69199999999999

Number of isotopes           2

Isotope label, isotopemass (u) and root mean square nuclear radius (fm)
10B       10.01293700000000    u        2.440000000000000    fm
11B       11.00930500000000    u        2.380000000000000    fm

Number of electrons           4

Nuclear mass for the isotopes
10B       10.01019410048500    u
11B       11.00656210048500    u

=============
 Lower state
=============

 Energy for infinite nuclear mass
         -24.29641300000000    H

 Energy corrected for normal mass effect
 10B     -24.29508157791551    H
 11B     -24.29520209876772    H

 Energy corrected for normal and specific mass effect
 10B     -24.29504731672334    H
 11B     -24.29517093906675    H

 Energy corrected for normal and specific mass effect and fieldshift
 10B     -24.29504570279576    H
 11B     -24.29516940353675    H

=============
 Upper state
=============

 Energy for infinite nuclear mass
         -23.98866800000000    H

 Energy corrected for normal mass effect
 10B     -23.98735344207112    H
 11B     -23.98747243637330    H

 Energy corrected for normal and specific mass effect
 10B     -23.98733747053996    H
 11B     -23.98745791066350    H

 Energy corrected for normal and specific mass effect and fieldshift
 10B     -23.98733589664331    H
 11B     -23.98745641321990    H
```

```
====================
 Energy differences
====================

 Energy difference between upper and lower state

 Difference for infinite nuclear mass

          0.3077450000000006    H

           67542.22021861674    cm-1

 Transition wavelength (Angstrom)
           1480.555416690861    A

 Differences with normal mass correction
 10B      0.3077281358443998    H
 11B      0.3077296623944186    H

 10B       67538.51896429451    cm-1
 11B       67538.85400329610    cm-1

 Transition wavelength (Angstrom)
 10B       1480.636554273079    A
 11B       1480.629209301059    A

 Wavelength difference between the isotopes
 10B 11B  7.3449720196094859E-03   A

 Differences with normal and specific mass correction
 10B      0.3077098461833820    H
 11B      0.3077130284032457    H

 10B       67534.50484769739    cm-1
 11B       67535.20326422669    cm-1

 Transition wavelength (Angstrom)
 10B       1480.724560363894    A
 11B       1480.709247424001    A

 Wavelength difference between the isotopes
 10B 11B  1.5312939893874500E-02   A


 Differences with normal and specific mass and field shift correction
 10B      0.3077098061524559    H
 11B      0.3077129903168476    H

 10B       67534.49606192466    cm-1
 11B       67535.19490522854    cm-1

 Transition wavelength (Angstrom)
 10B       1480.724752995960    A
```

```
11B        1480.709430695047    A

Wavelength difference between the isotopes
10B 11B  1.5322300912885113E-02   A
```

Part II

Large-scale active space calculations of isotope shifts

5 Introduction

The major problem in MCHF calculations is the selection of the configuration expansion. In accurate calculations it must be possible to estimate the uncertainty of a calculated parameter. Therefore, a whole series of calculations has to be done, where the configuration space is increased in a systematic way.

6 Active space approach

An efficient way of choosing the configuration expansion is to use an active set of radial orbitals. In this approach CSFs of a particular parity and LS symmetry are generated by excitations from one or more reference configurations to the active set. The active set of orbitals is then increased in a systematic way, allowing the convergence of calculated parameters to be studied. By imposing different restrictions on the way excitations can be done, orbitals can be targeted to describe different electron correlation effects. This idea has been utilized by quantum chemists in the restricted active space (RAS) approach for some time [12, 13]. By allowing only single (S) excitations from closed shells in the reference configuration, the orbitals in the active set will describe core-polarization effects. By allowing double (D) excitations, core-correlation in the pair-approximation can be described.

Generally, a good starting point for calculations is to include all single and double excitations to the active set from a few important reference configurations. This can be considered as the zero-order approximation. Since the specific mass shift operator couples configurations that differs with up to two electrons, it is necesarry to include triple (T) and quadruple (Q) excitations to improve the wavefunction further. When triple and quadruple excitations are included, the configuration expansion grows very rapidly with the increasing active set of orbitals, and it is in general only possible to include a small subset of these configurations. Another way of including certain triple and quadruple excitations is to use a multi-reference (MR) expansion. Here single and double excitations are made from a set of configurations with expansion coefficients larger than a certain cut-off. The convergence of the calculated parameter can then be studied with respect to the increasing size of the multi-reference set.

7 Active space studies of isotope shifts in boron

7.1 $1s^22s^2\ ^1S$ and $1s^22s2p\ ^1P$ in $B\ II$

If all excitations to the active set are allowed, the configuration expansion, refered to as the complete active space (CAS), grows very rapidly with the increasing active set. Many of these configurations, obtained mainly from triple and quadruple excitations, have very small expansion coefficients and contribute little to the total energy or to the studied parameters. It is therefore possible to impose restrictions on the allowed excitations, keeping the number of configuration states down, that result in only a very small change in the final result [14, 15].

In the calculations below (from reference [18]) only configurations where at least two of the orbitals have principal quantum numbers $n < 4$ were included. In Table I the value of the specific mass shift parameter, the electron density at the nucleus and the total energy, calculated from the zero-order Hamiltonian, for the ^1S term are shown as a function of the increasing active set of orbitals. It is seen that the specific mass shift parameter is converged to within 0.2 %. The final value $S = 0.597\ 09$ a.u. is in very good agreement with the value $S = 0.597\ 5$ a.u. of Chung *et al.* [16]. To see the effect of the imposed restrictions on the configuration expansion a CAS calculation was performed for the $5s4p3d2f1g$ orbital set. The change in the specific mass shift parameter compared with the restricted expansion is only 3×10^{-5} a.u. and is of no significance. In Table II the value of the specific mass shift parameter, the electron density at the nucleus and the total energy for the ^1P term are shown. The specific mass shift parameter changes with 0.5 % when going from the $6s5p4d3f2g1h$ to the $7s6p5d4f3g2h1i$ active set, indicating a little slower convergence for the ^1P term.

In Table III the mass and field shift corrected energies are shown for the ^{10}B and ^{11}B isotopes. The field shift corrections were calculated with root mean square nuclear radii; ^{10}B, $\langle r_N^2 \rangle^{1/2} =$ 2.44(6) fm and ^{11}B $\langle r_N^2 \rangle^{1/2} = 2.38(4)$ fm taken from pionic and muonic X-ray measurements [17]. It is seen, as expected for a light atom like boron, that the mass shift is the totally dominating effect. ¿From these energies the wavenumbers and wavelengths for the $1s^22s^2\ ^1S - 1s^22s2p\ ^1P$ transition were determined, the result is shown in Table IV. No experimental value of the isotope shift is known for this transition.

7.2 $1s^22s^22p\ ^2P$, $1s^22s^23s\ ^2S$ and $1s^22s2p^2\ ^2D$ in $B\ I$

Although neutral boron has only five electrons it remains a challange to calculate the isotope shift accurately. One of the reasons for this is the large and cancelling contributions to the SMS from the $1s$ and $2s$ shells. This type of cancelling effect is well known for the Fermi contact term where triple excitations change the degree of cancellation between the $1s$ and $2s$ shell contributions [19]. For SMS the situation is more difficult since the the SMS operator is a two-particle operator whereas the hfs operator is a one-particle operator. This means that in order to describe the degree of cancellation between the $1s$ and $2s$ shell contributions triple and quadruple excitations have to be included, leading to very large configuration expansions. Another problem is a number of near degeneracies occuring for all three terms studied. To yield quantitatively correct results excitations have to be made from all of these almost degenerate configurations.

Using a MR-MCHF approach where all SD excitations were made from the most important configurations a number of orbital basis sets were obtained. Three- and four-particle effects were then taken into account in large MR-CI calculations where SD excitations to the increasing active sets were done from all CSFs with expansion coefficients larger than 0.01. In Tables V-X the convergence of the SD-MR-MCHF and SD-MR-CI calculations are shown (from reference [20]). The correlation in the $1s$ shell is very important for the SMS. This can be seen from the CI calculations where only excitations from the outer shells to the active set were allowed. A comparison with the corresponding calculations were excitations from all shells were allowed shows that the contributions to the SMS from the CSFs describing the 1s and 2s shell correlation, respectively, are both large but partly cancelling. Thus, a small change in the 1s and 2s shell correlation, due to the inclusion of three and four-particle effects, can have a large influence on the total value of the SMS.

It is seen that the triple and quadruple excitations included in the MR-CI expansion increase the specific mass shift parameter of the ^2P term by more than 10 %. This change is even larger for the ^2D term where the increase is almost 50%. In Table XI the mass and field shift corrected energies are shown for the ^{10}B and ^{11}B isotopes. The wavenumbers and wavelengths for the $1s^22s^22p\ ^2P - 1s^22s^23s\ ^2S$ and $1s^22s^22p\ ^2P - 1s^22s2p^2\ ^2D$ transitions are shown in Table XII. Finally, the transition isotope shifts are compared with values from a third order MBPT calculation and experiment in Table XIII. The calculated isotope shift agrees very well with the experimental shift for both transitions. The present results are encouraging, showing that it is indeed possible to calculate isotope shifts for light atoms with high accuracy.

Since the Hubble Space Telescope was launched there has been an increasing interest in isotope shifts for light atoms due to the possibility of abundance and isotope composition determinations in astrophysical objects. For many transitions experimental data is not available, and the analysis of stellar spectra has to rely on computed isotope shifts [18]. It is reasonable to believe that large-scale MCHF and CI calculations will be of great importance for this work.

Acknowledgement

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Table I. The specific mass shift parameter, electron density at the nucleus and total energy (in a.u.) for the $1s^22s^2\ {}^1S$ term in *B II* as a function of the increasing active set of orbitals. The total energy has been calculated from the zero-order Hamiltonian. Ncfg is the number of configuration states in the wavefunction expansion.

active set	S (a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Ncfg
hf	0.000 00	72.629	-24.237 575	1
2s1p	-0.020 17	72.452	-24.296 413	5
3s2p1d	0.625 18	72.490	-24.334 812	63
4s3p2d1f	0.624 81	72.497	-24.342 409	460
5s4p3d2f1g	0.601 69	72.501	-24.346 046	1066
5s4p3d2f1g[a]	0.601 66	72.501	-24.346 052	2432
6s5p4d3f2g1h	0.598 03	72.503	-24.347 410	2306
7s6p5d4f3g2h1i	0.597 09	72.504	-24.347 943	4200

[a] Complete active space calculation. No restriction on the excitations.

Table II. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for the $1s^22s2p\ {}^1P$ term in *B II* as a function of the increasing active set of orbitals. The total energy has been calculated from the zero-order Hamiltonian. Ncfg is the number of configuration states in the wavefunction expansion.

active set	S (a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Ncfg
hf	-0.403 98	70.752	-23.912 873	1
2s1p	-0.401 07	70.748	-23.913 062	4
3s2p1d	0.291 44	70.692	-23.988 668	98
4s3p2d1f	0.256 36	70.714	-24.001 844	713
5s4p3d2f1g	0.277 32	70.712	-24.008 886	2300
5s4p3d2f1g[a]	0.277 34	70.712	-24.008 921	5654
6s5p4d3f2g1h	0.274 59	70.717	-24.011 624	5211
7s6p5d4f3g2h1i	0.273 30	70.719	-24.012 990	9772

[a] Complete active space calculation. No restriction on the excitations.

Table III. The mass and field shift corrected energies for the $1s^22s^2\ ^1S$ and $1s^22s2p\ ^1P$ terms in $B\ II$. The energies are given for the two stable isotopes ^{10}B and ^{11}B.

	$1s^22s^2\ ^1S$		$1s^22s2p\ ^1P$	
Energy	^{10}B	^{11}B	^{10}B	^{11}B
E_0	-24.347 943	-24.347 943	-24.012 990	-24.012 990
E_{nms}	-24.346 609	-24.346 730	-24.011 674	-24.011 793
$E_{nms+sms}$	-24.346 576	-24.346 700	-24.011 659	-24.011 780
$E_{nms+sms+fs}$	-24.346 575	-24.346 698	-24.011 658	-24.011 778

Table IV. Calculated spectroscopic data for the resonance transition in $B\ II$. The wavenumbers (σ) and wavelengths (λ) are given for the two stable isotopes ^{10}B and ^{11}B.

transition	$\sigma\ (cm^{-1})$	λ (Å)	isotope
$1s^22s^2\ ^1S - 1s^22s2p\ ^1P$	73505.735	1360.4381	^{10}B
	73506.453	1360.4248	^{11}B

Table V. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for $1s^22s^22p\ ^2P$ in $B\ I$ from SD-MR$\{1s^22s^22p, 1s^22p^3\}$ MCHF calculations.

n	S(a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Ncfg
hf	-0.404 86	71.921	-24.529 061	1
2	-0.410 51	71.785	-24.560 354	6
3	0.293 90	71.792	-24.621 891	129
4	0.240 37	71.862	-24.638 480	520
5	0.256 62	71.852	-24.645 478	1301
6	0.254 43	71.856	-24.648 728	2584
7	0.253 27	71.859	-24.650 290	4479
8	0.252 11	71.861	-24.651 009	7096
8[a]	-0.361 33	72.000	-24.601 789	988

[a] SD-MR$\{1s^22s^22p, 1s^22p^3\}$ CI calculation. $1s$ shell closed and excitations to the active set only allowed from the $2s$ and $2p$ shells in the multi-reference configurations.

Table VI. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for $1s^22s^22p\ ^2P$ in $B\ I$ from SD-MR-CI calculations as a fuction of the increasing active set of orbitals. The multi-reference set consisted of all CSFs with $c_j > 0.01$.

n	S(a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Ncfg
2	-0.410 51	71.785	-24.560 354	6
3	0.308 97	71.791	-24.622 672	366
4	0.258 53	71.864	-24.639 807	4 520
5	0.275 75	71.855	-24.647 000	16 525
6	0.274 12	71.859	-24.650 392	39 623
6[a]	0.274 12	71.859	-24.650 392	17 672
7[b]	0.273 34	71.861	-24.651 991	24 082
8[b]	0.272 32	71.863	-24.652 725	32 456

[a] The n=6 MR-CI expansion is condensed. Only CSFs with $c_j > 0.000001$ are included.

[b] CSFs obtained from SD excitations from $1s^22s^22p, 1s^22p^3$ and $1s^22s2p3d$ have been added to the condensed n=6 expansion.

Table VII. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for $1s^22s^23s\ ^2S$ in *B I* from SD-MR$\{1s^22s^23s, 1s^22p^23s, 1s^22s2p^2\}$ MCHF calculations.

n	S (a.u.)	$\|\psi(0)\|^2$	E_0 (a.u.)	Ncfg
hf	0.000 00	72.716	-24.352 104	1
3	0.640 20	72.461	-24.438 718	92
4	0.628 00	72.535	-24.456 608	379
5	0.625 71	72.540	-24.464 056	943
6	0.602 99	72.543	-24.467 945	1854
7	0.602 96	72.544	-24.469 218	3182
8	0.601 82	72.544	-24.469 860	4997
8[a]	-0.024 79	73.406	-24.420 083	635

[a] SD-MR$\{1s^22s^23s, 1s^22p^23s, 1s^22s2p^2\}$ CI calculation. $1s$ shell closed and excitations to the active set only allowed from the $2s$, $2p$ and $3s$ shells in the multi-reference configurations.

Table VIII. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for $1s^22s^23s\ ^2S$ in *B I* from SD-MR-CI calculations as a fuction of the increasing active set of orbitals. The multi-reference set consisted of all CSFs with $c_j > 0.01$.

n	S(a.u.)	$\|\psi(0)\|^2$	E_0 (a.u.)	Ncfg
3	0.640 36	72.461	-24.438 727	150
4	0.632 78	72.534	-24.456 917	1 734
5	0.631 31	72.539	-24.464 460	5 909
6	0.608 98	72.542	-24.468 409	13 431
7	0.609 50	72.543	-24.469 729	25 183
8	0.608 55	72.543	-24.470 389	41 987

Table IX. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for $1s^22s2p^2\ {}^2D$ in $B\ I$ from SD-MR$\{1s^22s2p^2, 1s^22s^23d\}$ MCHF calculations.

n	S(a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Ncfg
hf	-0.736 72	70.553	-24.311 869	1
2	-0.735 66	70.552	-24.311 921	4
3	-0.670 12	70.740	-24.379 506	157
4	-0.065 50	70.873	-24.416 497	812
5	-0.065 85	70.841	-24.424 768	2320
6	-0.066 09	70.819	-24.429 451	5004
7	-0.069 50	70.819	-24.431 353	9161
7[a]	-0.658 55	70.890	-24.382 926	1530

[a] SD-MR$\{1s^22s2p^2, 1s^22s^23d\}$ CI calculation. $1s$ shell closed and excitations to the active set only allowed from the $2s$, $2p$ and $3d$ shells in the multi-reference configurations.

Table X. The specific mass shift parameter, electron density at the nucleus and the total energy (in a.u.) for $1s^22s2p^2\ {}^2D$ in $B\ I$ from SD-MR-CI calculations as a fuction of the increasing active set of orbitals. The multi-reference set consisted of all CSFs with $c_j > 0.01$.

n	S(a.u.)	$\lvert\psi(0)\rvert^2$	E_0 (a.u.)	Ncfg
3	-0.668 34	70.740	-24.380 038	449
4	-0.039 40	70.878	-24.418 061	7 237
5	-0.039 01	70.846	-24.426 635	32 012
6[a]	-0.038 47	70.824	-24.431 399	21 674
7[a]	-0.041 36	70.824	-24.433 330	31 336

[a] The n=5 MR-CI expansion is condensed. Only CSFs with $c_j > 0.000001$ are included.
CSFs obtained from SD excitations from $1s^22s2p^2, 1s^22s^23d$ and $1s^22p^23d$ have been added to the condensed n=5 expansion.

Table XI. The mass and field shift corrected energies for the $1s^22s^22p\ ^2P$, $1s^22s^23s\ ^2S$ and $1s^22s2p^2\ ^2D$ terms in $B\ I$. The energies are given for the two stable isotopes ^{10}B and ^{11}B.

	$1s^22s^22p\ ^2P$		$1s^22s^23s\ ^2S$		$1s^22s2p^2\ ^2D$	
Energy	^{10}B	^{11}B	^{10}B	^{11}B	^{10}B	^{11}B
E_0	-24.652 725	-24.652 725	-24.470 389	-24.470 389	-24.433 330	-24.433 330
E_{nms}	-24.651 374	-24.651 496	-24.469 048	-24.469 169	-24.431 991	-24.432 112
$E_{nms+sms}$	-24.651 359	-24.651 483	-24.469 015	-24.469 139	-24.431 993	-24.432 114
$E_{nms+sms+fs}$	-24.651 358	-24.651 481	-24.469 013	-24.469 138	-24.431 992	-24.432 113

Table XII. Calculated spectroscopic data for the resonance transitions in $B\ I$. The wavenumbers (σ) and wavelengths (λ) are given for the two stable isotopes ^{10}B and ^{11}B.

transition	$\sigma\ (cm^{-1})$	λ (Å)	isotope
$1s^22s^22p\ ^2P - 1s^22s^23s\ ^2S$	40041.8532	2497.3869	^{10}B
	40041.6856	2497.3974	^{11}B
$1s^22s^22p\ ^2P - 1s^22s2p^2\ ^2D$	47850.5996	2089.8379	^{10}B
	47851.1788	2089.8127	^{11}B

Table XIII. Transition isotope shift for the resonance transitions. $\Delta\sigma = \sigma_{^{11}B} - \sigma_{^{10}B}$.

transition	$\Delta\sigma\ (cm^{-1})$	reference
$1s^22s^22p\ ^2P - 1s^22s^23s\ ^2S$	-0.168	MR-CI this work
	-0.094	MBPT
	-0.175	Experiment
$1s^22s^22p\ ^2P - 1s^22s2p^2\ ^2D$	0.579	MR-CI this work
	0.569	Experiment

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