Calculation of isotope shifts and relativistic shifts in CI, CII, CIII and CIV

J. C. Berengut

School of Physics, University of New South Wales, Sydney 2052, Australia

V. V. Flambaum

School of Physics, University of New South Wales, Sydney 2052, Australia and

Physics Division, Argonne National Laboratory,
Argonne, Illinois 60439-4843, USA

M. G. Kozlov

Petersburg Nuclear Physics Institute, Gatchina, 188300, Russia
(Dated: June 10, 2021)

Abstract

We present an accurate \textit{ab initio} method of calculating isotope shifts and relativistic shifts in atomic spectra. We test the method on neutral carbon and three carbon ions. The relativistic shift of carbon lines may allow them to be included in analyses of quasar absorption spectra that seek to measure possible variations in the fine structure constant $\alpha$ over the lifetime of the Universe. Carbon isotope shifts can be used to measure isotope abundances in gas clouds: isotope abundances are potentially an important source of systematic error in the $\alpha$–variation studies. These abundances are also needed to study nuclear reactions in stars and supernovae, and test models of chemical evolution of the Universe.

PACS numbers: 31.30.Gs, 06.20.-f, 31.25.Jf
Keywords: isotope shift; mass shift; relativistic shift; carbon

*Electronic address: jcb@phys.unsw.edu.au
I. INTRODUCTION

Recent studies of quasar absorption systems have suggested that the fine structure constant, $\alpha = e^2/\hbar c$, may have been smaller in the early universe than it is today on Earth [1, 2, 3, 4]. Other groups using different telescopes have shown zero variation [5, 6, 7]. All of these studies use the “many multiplet” method [8], which relies on the comparison of the wavelengths of many transitions in many ions to enhance the size of the effects and remove sources of systematic error. While this method offers an order-of-magnitude improvement in sensitivity over the previously used alkali-doublet method, a potential systematic error is introduced related to the isotope abundances of the absorbers. If the isotope abundances of the absorbers differ from the terrestrial abundances then there can be spurious shifts in the measured wavelengths which may be incorrectly interpreted as variation of $\alpha$.

This problem can be resolved if both the relativistic shift and isotope shift of each transition is known, by using particular combinations of the transition frequencies as probes which are insensitive to either $\alpha$-variation or isotopic abundances [9]. Changes in the isotope abundances and the fine-structure constant can then be measured directly.

The measured isotopic abundance of carbon can be used to test models of chemical evolution of the Universe. Of particular importance are some chemical evolution models with enhanced populations of intermediate-mass stars that serve as factories for heavy Mg isotopes. The changes in the relative abundances of Mg isotopes could account for much of the evidence for variation in $\alpha$ at relatively low redshifts ($z \lesssim 2$) [10, 11]. However, these models also overproduce nitrogen, violating observed abundance trends in high-$z$ damped Lyman-\(\alpha\) systems. Furthermore, it has been shown that such models would also increase the ratio of $^{13}\text{C}$ to $^{12}\text{C}$ [12]. With the isotope shifts calculated in this paper it is possible to measure this ratio, and hence provide a diagnostic of these non-standard chemical evolution models.

We also have one more reason to study carbon: it is a well studied atom, and we can compare the results of our method with those of other theoretical analyses, as well as a few experiments (unfortunately, isotope shifts for the majority of lines used in astrophysical applications have not been measured). In particular, much progress has been made to calculate isotope shifts using the multiconfigurational Hartree-Fock (MCHF) and configuration interaction (CI) approach [13, 14, 15, 16]. In Sections II and III we present our method of calculating the isotope shift. It uses the finite-field method to reduce the problem of isotope shift (or relativistic shift) to that of an energy calculation. The transition energies are calculated using a combination of the configuration interaction and many-body perturbation theory (MBPT) approaches, following the works of Refs. [17] and [18].

In Sec. IV we show that our CI + MBPT method has accuracy comparable to that of the MCHF calculations, and are accurate enough to be used to measure isotope abundances. We believe that our method may have some advantages over the MCHF calculations; in particular, it is more readily applicable to heavier atoms (where we need to calculate isotope shifts for the study of the $\alpha$ variation and isotopic evolution) and has already been shown to be more accurate in the case of Mg I [19]. We also use this method to calculate dependence of the carbon transition frequencies on $\alpha$, which is needed to study $\alpha$ variation.
II. METHOD

Using many-body perturbation theory in the residual Coulomb operator and specific mass shift (SMS) operator to calculate isotope shift shows poor convergence. Therefore, we are looking for an “all order” method of calculation. The finite-field scaling method is used, reducing the task to an energy calculation, and including the SMS in all parts of the calculation. A similar idea is used to calculate relativistic shift.

A. Relativistic shift

To measure \( \alpha \) in the distant past, we compare the frequency of transitions in the laboratory, \( \omega_0 \), with those measured in the quasar absorption spectra, \( \omega \). The difference can be expressed as

\[
\omega = \omega_0 + qx, \tag{1}
\]

where \( x = (\alpha/\alpha_0)^2 - 1 \) and \( \alpha_0 \) is the laboratory value of the fine structure constant. We vary \( \alpha \) directly in computer codes, and extract the relativistic shift \( q \) from the calculated spectrum as

\[
q = \frac{d\omega}{dx}_{x=0}. \tag{2}
\]

Thus we have reduced the problem to an accurate numerical calculation of the energy, and hence \( \omega \).

B. Isotope shift

The isotope shifts of atomic transition frequencies come from two sources: the finite size of the nuclear charge distribution (the “volume” or “field” shift), and the finite mass of the nucleus (see, e.g., Ref. [20]). In atoms as light as carbon, the field shift is negligible in comparison to the mass shift: we will not consider it further.

Because a real nucleus has a finite mass, there is a recoil effect from the movements of the electrons. The energy shift due to the recoil of the nucleus of mass \( M \) is given by

\[
\frac{p_N^2}{2M} = \frac{1}{2M} \left( \sum_i p_i \right)^2 = \frac{1}{2M} \sum_i p_i^2 + \frac{1}{M} \sum_{i<j} p_i \cdot p_j. \tag{3}
\]

This “mass shift” is traditionally divided into the normal mass shift (NMS) and the specific mass shift (SMS), given by the first and second terms of Eq. (3), respectively. The normal mass shift is easily calculated from the transition frequency; the specific mass shift is difficult to evaluate accurately.

The shift in energy of any transition in an isotope with mass number \( A' \) with respect to an isotope with mass number \( A \) can be expressed as

\[
\delta \nu^{A',A} = \nu^{A'} - \nu^A = (k_{\text{NMS}} + k_{\text{SMS}}) \left( \frac{1}{A'} - \frac{1}{A} \right), \tag{4}
\]
where the normal mass shift constant is

\[ k_{\text{NMS}} = -\frac{\nu}{1823}. \] (5)

The value 1823 refers to the ratio of the atomic mass unit to the electron mass.

To calculate \( k_{\text{SMS}} \) we include a scaled specific-mass-shift operator directly into our energy calculation from the very beginning. We add the two-body SMS operator to the Coulomb potential \( \tilde{Q} = 1/|r_1 - r_2| + \lambda \mathbf{p}_1 \cdot \mathbf{p}_2 \). The operator \( \tilde{Q} \) replaces the Coulomb operator everywhere that it appears in an energy calculation. We recover the specific mass shift constant as

\[ k_{\text{SMS}} = \frac{d\omega}{d\lambda}|_{\lambda=0}. \] (6)

The operator \( \tilde{Q} \) has the same symmetry and structure as the Coulomb operator (see Appendix A).

### III. ENERGY CALCULATION

To calculate the energies we first solve the Dirac-Fock equations for the core and valence electrons, and we generate a basis set that includes the core and valence orbitals and a number of virtual orbitals. We then calculate the energy levels using a combination of CI and MBPT for many-valence-electron atoms as was done for Mg I in Ref. [19]. In this section we outline the procedure for the combined CI and MBPT method; it generally follows the work of Ref. [17]. Note that for single-valence-electron atoms, where the CI procedure is unnecessary, the method reduces to the addition of core-correlation effects to the Dirac-Fock energy using MBPT, as was shown to be highly successful for calculating SMS in Ref. [21].

Atomic units \((\bar{\hbar} = m_e = e = 1)\) are used throughout this paper.

#### A. Single particle basis

We firstly solve the Dirac-Fock equations for one-particle wavefunctions of the open-shell core \(|m\rangle\)

\[ h^{\text{DF}} |m\rangle = \epsilon_m |m\rangle, \] (7)

where

\[ h^{\text{DF}} = c \mathbf{\alpha} \cdot \mathbf{p} + (\beta - 1)m_e c^2 - \frac{Z}{r} + V^{\text{NDF}}(r) \] (8)

where \( V^{\text{NDF}} \) is the potential (both direct and exchange) of the \( N_{\text{DF}} \) electrons included in the self-consistent Hartree-Fock procedure. Note that this is not necessarily the number of electrons in the closed-shell core, in fact \( N_{\text{core}} \leq N_{\text{DF}} \leq N \), where \( N \) is the total number of electrons. For the purposes of the CI calculation there are \( N - N_{\text{core}} \) valence electrons.

We need to generate a basis set, \(|i\rangle\) that includes the core and valence states and a large number of virtual states. In this paper we have used a B-spline basis set, formed by diagonalizing the Dirac-Fock operator on the basis set of B-splines and excluding orbitals with high energy. This basis has been shown to be effective in energy calculations using this method of CI and MBPT [18].
B. Configuration interaction method

The many-electron Hilbert space is separated into subspaces $P$ and $Q$. $P$ corresponds to the frozen-core approximation; $Q$ is complimentary to it and includes all states with core excitations. Using Slater determinants (denoted with capital letters) $|I\rangle$ of the single-particle functions $|i\rangle$ as a basis set in the many-electron space, we can define projection operators for $P$ and $Q$ by

$$P = \sum_{I \in P} |I\rangle \langle I|$$

$$P + Q = 1$$

Determinants that have all core states fully occupied are in the $P$ subspace; all others are in the subspace $Q$.

In the CI method, the many-electron wavefunction is expressed as a linear combination of Slater determinants from the subspace $P$:

$$\psi = \sum_{I \in P} C_I |I\rangle,$$

where the $C_I$ are obtained from the matrix eigenvalue problem

$$\sum_{J \in P} H_{IJ} C_J = E C_I.$$

In the frozen-core approximation, the determinants $|I\rangle$ need include only the valence electrons. Although $P$ is infinite-dimensional, we can use a finite-dimensional model subspace by specifying the set of allowed configurations for the valence electrons, for example by restricting the set of single particle states. The restrictions we use are different for each ion, and are expressed more fully in the relevant parts of Section IV. We will not distinguish here between the finite and infinite subspaces.

The Hamiltonian for the CI problem is a projection of the exact Hamiltonian $H$ onto the model subspace. The core is frozen in the $P$ subspace, so our projected Hamiltonian is

$$\mathcal{P}H\mathcal{P} = E_{\text{core}} + \sum_{i>N_{\text{core}}} h_{i}^{\text{CI}} + \sum_{j>i>N_{\text{core}}} \frac{1}{r_{ij}},$$

where $E_{\text{core}}$ is the total energy of the $N_{\text{core}}$ core electrons and the single particle operator

$$h^{\text{CI}} = c \alpha \cdot p + (\beta - 1)m_{e}c^{2} - \frac{Z}{r} + V^{N_{\text{core}}}$$

acts only on the valence electrons. Using the operator (13) in Eq. (12) corresponds to the pure CI method in the frozen-core approximation.

C. Exact Hamiltonian expansion

We wish to write the exact equivalent of $H$ in the subspace $P$. The “Feshbach operator” yields the exact energy when operating on the model function $\Psi_{P} = \mathcal{P}\Psi$. Following Lindgren and Morrison [22], we start from the many-body Schrödinger equation in the form

$$\mathcal{H}(\mathcal{P} + \mathcal{Q})\Psi = E\Psi$$

(15)
and operate from the left with $P$ and $Q$, respectively to obtain

$$
\begin{align*}
\mathcal{P}\mathcal{H}\mathcal{P}\Psi_P + \mathcal{P}\mathcal{H}\mathcal{Q}\Psi_Q &= E\Psi_P \\
\mathcal{Q}\mathcal{H}\mathcal{P}\Psi_P + \mathcal{Q}\mathcal{H}\mathcal{Q}\Psi_Q &= E\Psi_Q.
\end{align*}
$$

Eliminating $\Psi_Q$,

$$
[\mathcal{P}\mathcal{H}\mathcal{P} + \Sigma(E)]\Psi_P = E\Psi_P
$$

where

$$
\Sigma(E) = \mathcal{P}\mathcal{H}\mathcal{Q}\frac{1}{E - \mathcal{Q}\mathcal{H}\mathcal{P}}\mathcal{Q}\mathcal{H}\mathcal{P}.
$$

In Ref. [17] these expressions were also used to rewrite the orthonormality conditions for the solutions of Eq. (15) in terms of the model functions $\Psi_P$ (the solutions of Eq. (10)). As they found however, if an appropriate choice of the $P$ subspace is made, the usual orthonormality condition for $\Psi_P$ can be applied. In this case the standard CI procedure can be used to solve Eq. (16).

D. Many-body perturbation theory

Here we will generate a perturbation expansion for $\Sigma$. Define a single particle Hamiltonian by

$$
h_0 a_i^\dagger |0\rangle = \epsilon_i a_i^\dagger |0\rangle
$$

where we introduce the operators $a_i^\dagger$ ($a_i$) to create (annihilate) a particle. For particles in the core, the functions are those of Eq. (7). The many-body zero-order Hamiltonian is

$$
\mathcal{H}_0 = E_{\text{core}} + \sum_i \{a_i^\dagger a_i\} \epsilon_i.
$$

where the brackets $\{\ldots\}$ denote normal ordering with respect to the closed-shell core.

The exact Hamiltonian is

$$
\mathcal{H} = \sum_i h^{\text{mac}} + \sum_{ij} \frac{1}{r_{ij}}
$$

where $h^{\text{mac}} = c\boldsymbol{\alpha} \cdot \boldsymbol{p} + (\beta - 1)mc^2 - \frac{Z}{r_i}$. $\mathcal{H}$ can be separated into zero, one, and two-body parts:

$$
\begin{align*}
\mathcal{H}^{(0)} &= E_{\text{core}} \\
\mathcal{H}^{(1)} &= \sum_{ij} \{a_i^\dagger a_j\} \left[ \langle i | h^{\text{mac}} | j \rangle \\
&\quad + \sum_{m} \left( \langle im | r_{12}^{-1} | jm \rangle - \langle im | r_{12}^{-1} | mj \rangle \right) \right] \\
&= \sum_{ij} \{a_i^\dagger a_j\} \langle i | h^{\text{CI}} | j \rangle \\
\mathcal{H}^{(2)} &= \sum_{ijkl} \{a_i^\dagger a_j^\dagger a_l a_k\} \langle ij | r_{12}^{-1} | kl \rangle.
\end{align*}
$$
Expanding Eq. (17) in the residual Coulomb interaction, \( V = H - H_0 \), we obtain

\[
\Sigma(E) = \mathcal{P}\mathcal{H}\mathcal{Q}\frac{1}{E-H_0} \mathcal{Q}\mathcal{H}\mathcal{P} \\
+ \mathcal{P}\mathcal{H}\mathcal{Q}\frac{1}{E-H_0} \mathcal{Q}V\mathcal{Q}\frac{1}{E-H_0} \mathcal{Q}\mathcal{H}\mathcal{P} + \ldots
\] (23)

One advantage of this formalism is that \( h_0 \) is not necessarily the same as \( h^{DF} \). Thus we may in principle use any set of functions we like in the virtual basis as long as they are orthogonal. In practice, however, it is important that \( V \) not get too large, and this requires that

\[
V^{(1)} = \langle i | h^{CI} - h_0 | j \rangle
\] (24)

is small.

We can write \( \Sigma \) in matrix form:

\[
\Sigma_{IJ} = \sum_{M \in Q} \frac{\langle I | H | M \rangle \langle M | H | J \rangle}{E - E_M} \\
+ \sum_{M,L \in Q} \frac{\langle I | H | M \rangle \langle M | V | L \rangle \langle L | H | J \rangle}{(E - E_M)(E - E_L)} + \ldots
\] (25)

\[
\Sigma_{IJ} = (\Sigma_2)_{IJ} + (\Sigma_3)_{IJ} + \ldots
\] (26)

where I and J enumerate determinants from the subspace \( P \), and M and L are determinants from the subspace \( Q \).

In this paper we calculate \( \Sigma \) to second-order of the perturbation expansion. For the one-valence-electron case it has been shown that this level of perturbation theory, when used with the finite-field scaling method, is sufficient to obtain accurate results for isotope shift [21]. Furthermore, previous studies have shown that energies calculated to this order are very accurate [17, 18].

Substituting \( \Sigma_2 \) into (16) we obtain the equation of the combined CI and MBPT method, which we write in the same form as Eq. (12):

\[
\sum_{J \in P} \left( H_{IJ} + \sum_{M \in Q} \frac{\langle I | H | M \rangle \langle M | H | J \rangle}{E - E_M} \right) C_J = EC_I.
\] (27)

Thus our method includes the core-correlation effects by simply altering the matrix elements in the CI calculation. In practice, this involves adding the matrix element of the sigma operator to the one and two-particle Coulomb integrals.

E. Diagrammatic technique for calculating \( \Sigma \)

Here we present all second-order diagrams for \( \Sigma \), represented by Goldstone diagrams (see, e.g.: Ref. [22]). The diagrams are valid for any ion and any choice of core. Unlinked lines are omitted, since they correspond to states of the valence electrons that are not involved in the interaction. The omitted lines do affect the value of the MBPT correction via the Pauli principle; however, as noted in Ref. [17], the Pauli principle can be ignored due to the exact cancellation of unphysical terms in different diagrams. This rule works for all orders of perturbation theory (this is Wick’s theorem, see e.g.: Ref. [22]).
The second-order diagrams can be grouped according to how many external lines (valence electrons) they have. There are four one-valence-electron diagrams, all shown in Fig. 1. They correspond to the “self-energy” correction, which describes correlations between the valence electron and the core. Additionally, there are five so-called “subtraction diagrams” for the self-energy. These are diagrams that involve the external field $\mathcal{V}^{(1)}$ (Eq. (24)), and are so named because in the Hartree-Fock field enters $\mathcal{V}^{(1)}$ with a minus sign. In our formulation we instead use $\mathcal{H}^{(1)}$ as the external field (see Eqs. (21) and (25)) which is equivalent when calculating $\Sigma_2$ because $\mathcal{P}\mathcal{H}_0\mathcal{Q} = 0$. Three of the $\Sigma^{(1)}$ subtraction diagrams are shown in Fig. 2; the other two are the mirror image partners of diagrams 2.1 and 2.2.

FIG. 1: One-valence-electron diagrams of $\Sigma$ ($\Sigma^{(1)}$).

FIG. 2: Subtraction diagrams of $\Sigma^{(1)}$. Diagrams 1 and 2 have complementary diagrams obtained by reflection in the vertical plane.

Diagrams with two external lines correspond to screening of the valence-valence interaction by the core electrons. There are nine diagrams represented in Fig. 3 and four subtraction diagrams represented in Fig. 4. The resulting corrections to the interactions between valence electrons can be written in the form of an effective radial integral, as is usually done for the Coulomb integrals. However, it is important to note that the box diagrams (Figs. 3.4 - 3.6) have less symmetry than the Coulomb integrals, because swapping the initial and final states in either the upper or lower lines changes the integral. This approximately doubles the number of independent radial integrals that need to be stored for the CI problem. In addition, for the box diagrams the multipolarity of the Coulomb interaction need not follow the usual rule: $\xi(l_a + l_c + k)\xi(l_b + l_d + k)$ (see Appendix A). Instead, $k$ need only satisfy the triangle conditions and can be both odd and even. This would again double the number of independent radial integrals, except that we have found that the diagrams of “wrong” parity are unimportant for carbon and may be omitted in order to reduce the complexity of the calculations.
FIG. 3: $\Sigma^{(2)}$: Diagrams 1, 2 and 3 have complementary diagrams obtained by reflection in the vertical plane.

FIG. 4: $\Sigma^{(2)}$ subtraction diagrams. Each has a complementary mirror-image partner.

It is worth noting also that the two-body diagrams with the largest contribution to the energy (the direct diagram, Fig. 3.1, and its mirror) make no (linear) contribution to the SMS because they cancel. The exchange diagrams do contribute to the SMS; nevertheless, it is because of this cancellation that the contribution of $\Sigma^{(2)}$ to $k_{\text{SMS}}$ is generally smaller than that of $\Sigma^{(1)}$.

Figure 5 shows a diagram with three external lines, $\Sigma^{(3)}$, where three valence electrons interact via the core. The diagrams of this type are easy to calculate (having only one internal summation and no summations over virtual states), but the number of corresponding effective radial integrals is huge. To include this diagram everywhere in the CI calculation would involve taking into account not only corrections to $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(2)}$, but it would also introduce an effective $\mathcal{H}^{(3)}$. Fortunately, as explained in Ref. [17], it is possible to omit these diagrams entirely provided that one makes an appropriate choice of the atomic core. We have not included $\Sigma^{(3)}$ in this paper.
FIG. 5: Effective three-valence-electron interaction of Σ$_2$.

Analytical expressions for the diagrams of Figs. 1–4 are given in Appendix B.

A final point worth mentioning is the definition of the energy denominators in the expressions corresponding to the diagrams. Our formalism corresponds to Brillouin-Wigner perturbation theory, and so there is an explicit dependence on the energy of the whole atom: $E$ in Eqs. (17) and (27).

From Eq. (13), $E = E_{\text{core}} + E_{\text{val}}$, and so the core part cancels in the energy denominator $E - H_0$ (see Eq. (23)). The energy $E_{\text{val}}$ corresponds to the energy of all the valence electrons. To calculate $H_0$, however, one should take into account the state of all valence electrons for each disconnected diagram. This is computationally impractical, but again one can simplify. In this paper all connected diagrams are evaluated at the energies which correspond to the main configuration. For example, when calculating Fig. 1.1 the usual Rayleigh-Schrödinger perturbation theory would give the denominator $(\epsilon_a + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)$; we instead use $(\epsilon_{2s} + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)$ if $a$ and $b$ are $s$-wave, or $(\epsilon_{2p_{1/2}} + \epsilon_n - \epsilon_\alpha - \epsilon_\beta)$ if $a$ is $p$-wave, and so on.

The Brillouin-Wigner formalism used in our method has two major advantages over the Rayleigh-Schrödinger perturbation theory. Firstly, we wish to preserve the symmetry of the CI matrix when Σ is added, so we cannot have an energy denominator that depends on which state is initial and which is final. Secondly, Rayleigh-Schrödinger theory does not allow a large $P$ space as it will produce small denominators for excited configurations. That is known to lead to “intruder states” — unphysical states that can lie even below the ground state. By contrast, Brillouin-Wigner theory is known to have the wrong limit for an infinite number of valence electrons. It is possible to formulate the theory without these drawbacks by modifying $E$ (Ref. [23]). However, the energy dependence of the effective Hamiltonian is a higher order effect; compared to the prescription above, it leads to a relatively small energy correction that we neglect.

**IV. CALCULATIONS AND RESULTS**

We present results for each species of carbon separately, in order of increasing number of valence electrons. For all calculations we use a relativistic B-spline single-electron basis set similar to that developed by Johnson et al. [24, 25, 26]. In all cases the MBPT calculation considers $1s^2$ as the core, and all other states as valence. We have used two different B-spline basis sets, each with a different number of shells included in the self-consistent Dirac-Fock procedure. The first set, $B_1$, is formed in the potential of the closed shell $1s^2$ core; this corresponds to $N_{DF} = N_{\text{core}}$. For this set the subtraction diagrams of Figs. 2 and 4 are zero.
The second basis set, $B_2$, is formed in the potential of the $1s^22s^2$ core; thus $N_{DF} > N_{core}$ and the subtraction diagrams must be included.

The basis sets are described by giving the largest principal quantum number for each wave, e.g. $8spd6f$ includes the orbitals $1-8s_{1/2}$, $2-8p_j$, $3-8d_j$, and $4-6f_j$. For the MBPT we have used the basis $40spdfg$ for all ions. This basis is fully saturated in the sense that the energies and isotope shifts do not change with the addition of more basis functions.

A. CIV

CIV has one electron above a closed $1s^2$ core. It can therefore be treated as a single valence electron atom using MBPT, or as a three electron atom using CI. We have used both methods; the results are presented for comparison in Table I. In each case, the calculations were done using the $B_1$ basis set. The isotope shift results have also been compared with previous theoretical approaches. Multiconfiguration Hartree-Fock – CI calculations were presented in Ref. [13], which also combined the Hylleraas and full-core plus correlation (FCPC) calculations of Refs. [27] and [28] respectively.

| Level | Energy DF + $\Sigma^{(1)}$ Full CI Other works (expt.) | Energy (cm$^{-1}$) | $k_{SMS}$ (GHz·amu) |
|-------|-----------------------------------------------------|-------------------|-------------------|
| $2p \ ^2P_{1/2}^o$ | 64592 | 64594 | 64594$^a$ |
| $2p \ ^2P_{3/2}^o$ | 64592 | 64594 | 64594$^a$ |
| $2p \ ^2P_{1/2}^o$ | 64511 | -4521 | -4526$^a$ |
| $2p \ ^2P_{3/2}^o$ | 64504 | -4514 | -4527$^b$ |
| $k_{SMS}$ (GHz·amu) | 64449$^c$ | 64449$^c$ | 64449$^c$ |

$^a$MCHF–CI: Carlsson et al., 1995 [13]
$^b$MCHF: Godefroid et al., 2001 [14]
$^c$Hylleraas + FCPC: Results of King, 1989 [27], and Wang et al., 1993 [28], combined and presented in Ref. [13]

As noted previously, the MBPT basis was completely saturated, however we have only included second order diagrams in our calculation. By contrast, the CI calculations are complete (although they do not include the Breit interaction and QED effects), but the basis is not completely saturated. We have used an effective $22spdf$ basis for the CI calculation, including only single and double excitations from the leading configurations (SD-CI). We included triple excitations for a smaller basis, $14spdf$: this made a difference of less than 2 cm$^{-1}$ in the transition energy, and less than 1 GHz·amu for $k_{SMS}$. Other $f$-wave and higher partial waves were also found to be unimportant.
All methods give the same value for the transition energies and SMS constants to within 0.5%.

B. CIII

The ground state for CIII is 1s²2s 1S₂. We have done our calculations both as a four-electron CI problem (full CI) and by combining two-valence-electron CI with MBPT, considering 1s² as the frozen core (CI + Σ⁽¹⁾). All results are presented in Table II. Also included are CI results (the pure two-electron CI method) and CI + Σ⁽¹⁾ results (that do not include Σ⁽²⁾). This allows us to examine the roles of the different parts of the core-correlation. The CI and CI + Σ⁽¹⁾ results are calculated with the B₄ basis set; the complete CI + Σ⁽¹⁾,₂ results have been calculated using both the B₁ and B₂ sets. Additionally we have presented the MCHF results of Ref. [15].

TABLE II: Comparison of energies, kSMS, and q-values for transitions from the ground state in CIII using various methods. Note that the MCHF results are non-relativistic and hence do not distinguish fine-structure.

| Level       | Energy CI CI + Σ⁽¹⁾ CI + Σ⁽¹⁾,₂ Full CI MCHFᵃ       |
|-------------|-----------------------------------------------------|
|             | Energy (cm⁻¹) B₂ B₁                                  |
| 2s2p 3P₀ ⁰  | 52367 52750 52322 52349 52383 52506 52280           |
| 2s2p 3P₁ ⁰  | 52391 52784 52357 52383 52418 52534               |
| 2s2p 3P₂ ⁰  | 52447 52852 52427 52453 52488 52592               |
| 2s2p 1P₀ ¹  | 102352 103719 103365 102725 102775 103109 102598   |
| 2s2p 3P₀ ⁰  | -3439 -3478 -3473 -3470 -3483 -3475                |
| 2s2p 3P₁ ⁰  | -3438 -3476 -3472 -3468 -3480                      |
| 2s2p 3P₂ ⁰  | -3434 -3473 -3468 -3465 -3474                      |
| 2s2p 1P₀ ¹  | -2688 -2759 -2790 -2784 -2882 -2817               |
| 2s2p 3P₀ ⁰  | 75 74 74                                          |
| 2s2p 3P₁ ⁰  | 109 108 108                                        |
| 2s2p 3P₂ ⁰  | 177 178 178                                        |
| 2s2p 1P₀ ¹  | 165 165 165                                        |

ᵃJönsson et al., 1999 [15]

For the full four-electron CI method we used a very large basis 16spd⁹, in the SD-CI approximation. This was not enough to saturate the basis entirely, and we could go no further because the Hamiltonian matrix became too large. The error in kSMS from the full CI calculation could be as large as 100 GHz·amu. Nonetheless, they are in agreement with the calculations of Ref. [15], as well as the results of our own CI + MBPT.

The CI + MBPT method is particularly accurate for CIII for two reasons. Firstly, because there are only two valence electrons there are no triple excitations, which keeps the
Hamiltonian small without the need for approximations (for ions with more valence electrons we have used the SD-CI approximation). Because the Hamiltonian is relatively small, we can completely saturate the basis at 20spdf. Also, there is no $\Sigma^{(3)}$ (corresponding to Fig. 5); as stated before, in this paper we have not included it anyway. These points hold true for all two-valence-electron atoms; in particular we have previously shown that excellent results are attainable for Mg I (Ref. [19]).

In Ref. [15] the MCHF results were given an error of 1%; our CI + MBPT results are within this range, and so we believe that we have obtained a similar accuracy. It is also worth noting again that we have excluded the extra box diagrams with “wrong” parity from the results presented. The inclusion of these diagrams in $\Sigma^{(2)}$ makes a difference of around 0.1% to the $k_{\text{SMS}}$ constants.

C. C II

We have treated C II as a three-valence-electron ion; its ground state is $2s^2 2p \, ^3P^o_{1/2}$. We have used the $B_2$ basis 20spdf, which corresponds to the $V^{N-1}$ potential, and we have restricted ourselves in the CI problem to single and double excitations from the leading configurations $2s^22p$ and $2s2p^2$.

In Table III we present all results for C II. Again we have presented the breakdown of the various parts of the CI + MBPT method. We have also performed our calculations using the $B_1$ basis: this changed the results by less than 1% for all results except for the $^2S_{1/2}$ transition, in which the difference was around 3%. For this transition, neither basis set was enough to completely saturate $k_{\text{SMS}}$. Furthermore, the difference between the results of CI + MBPT and MCHF–CI is fairly large for this transition (around 7%). Adding the next most important configuration, $2s^23s$, to the leading set changes the energy of the $^2S_{1/2}$ transition by 30 cm$^{-1}$ (0.03%) and $k_{\text{SMS}}$ by 14 GHz·amu (around 1%). The effect on all other transitions was much smaller.

D. C I

In Table IV we present energies for transitions in neutral carbon. The ground state of C I is $2s^22p^2 \, ^3P_0$. We used the $B_2$ basis of size 16spdf, and took all single and double excitations from several leading configurations. The energies obtained for this atom are not as good as those of the other ions. It is testimony to the power of the B-spline basis, however, that the levels appear in the correct order (with the exception of some fine structure), which is remarkable considering that the spectrum is very dense.

We have generated $q$-values for C I because the previous calculations (Ref. [29]) had large uncertainties. We believe the new values, presented in Table IV, have errors of around 10 cm$^{-1}$.

In Table V we present the SMS constants for C I. We are within 1% of the values obtained using the MCHF–CI method (Refs. [13] and [16]). For most transitions the effect of core-correlations on $k_{\text{SMS}}$ is around 1 or 2%, however in some cases they are larger (for example, in $2s2p^3 \, ^3P^o$ the core correlations are 8% of the total).
TABLE III: Comparison of energies, $k_{\text{SMS}}$, and $q$-values for transitions from the ground state in CII. Note that the MCHF–CI results are non-relativistic and hence do not distinguish fine-structure.

| Level | Energy (expt.) | This work | MCHF–CI | CI $\Sigma(1)$ | CI $\Sigma(1,2)$ |
|-------|----------------|-----------|----------|----------------|------------------|
| $2s^2p^2 \, ^4P_{1/2}$ | 43003 | 43118 | 42767 | 42782 |
| $2s^2p^2 \, ^4P_{3/2}$ | 43025 | 43144 | 42794 | 42808 |
| $2s^2p^2 \, ^4P_{5/2}$ | 43054 | 43186 | 42838 | 42852 |
| $2s^2p^2 \, ^2D_{5/2}$ | 74930 | 75587 | 75350 | 75227 | 74842 |
| $2s^2p^2 \, ^2D_{3/2}$ | 74933 | 75585 | 75347 | 75225 |
| $2s^2p^2 \, ^2S_{1/2}$ | 96494 | 97095 | 96965 | 96960 | 96478 |
| $2s^2p^2 \, ^2P_{1/2}$ | 110624 | 112135 | 111913 | 111205 | 110569 |
| $2s^2p^2 \, ^2P_{3/2}$ | 110666 | 112187 | 111967 | 111259 |

$k_{\text{SMS}}$ (GHz·amu)

| Level | $k_{\text{SMS}}$ |
|-------|------------------|
| $2s^2p^2 \, ^4P_{1/2}$ | -2913 |
| $2s^2p^2 \, ^4P_{3/2}$ | -2912 |
| $2s^2p^2 \, ^4P_{5/2}$ | -2910 |
| $2s^2p^2 \, ^2D_{5/2}$ | -2604 |
| $2s^2p^2 \, ^2D_{3/2}$ | -2604 |
| $2s^2p^2 \, ^2S_{1/2}$ | -1204 |
| $2s^2p^2 \, ^2P_{1/2}$ | -1323 |
| $2s^2p^2 \, ^2P_{3/2}$ | -1320 |

$q$ (cm$^{-1}$)

| Level | $q$ |
|-------|-----|
| $2s^2p^2 \, ^4P_{1/2}$ | 132 |
| $2s^2p^2 \, ^4P_{3/2}$ | 157 |
| $2s^2p^2 \, ^4P_{5/2}$ | 200 |
| $2s^2p^2 \, ^2D_{5/2}$ | 179 |
| $2s^2p^2 \, ^2D_{3/2}$ | 176 |
| $2s^2p^2 \, ^2S_{1/2}$ | 165 |
| $2s^2p^2 \, ^2P_{1/2}$ | 162 |
| $2s^2p^2 \, ^2P_{3/2}$ | 215 |

$^a$Jönsson et al., 1996 [16]
$^b$Berengut et al., 2004 [29]

V. CONCLUSIONS

In this paper we have presented, in detail, a method for calculating isotope shifts and relativistic shifts in atomic spectra. The method uses the finite-field method to reduce the problem to that of an energy calculation, which is carried out using CI for the valence electrons combined with MBPT for the core correlations. Having previously tested the method in magnesium, we have now applied it to transitions in neutral carbon, CII, CIII, and CIV. In all cases we have agreement with previous MCHF and MCHF–CI calculations to
TABLE IV: Comparison of energies and $q$-values for transitions from the ground state in CI using various methods. Note that the MCHF–CI results are non-relativistic and hence do not distinguish fine-structure.

| Level                    | Energy (cm$^{-1}$) | $q$ (cm$^{-1}$) |
|--------------------------|--------------------|----------------|
|                          | (expt.) CI CI + $\Sigma^{(1)}$ CI + $\Sigma^{(1,2)}$ MCHF–CI CI + $\Sigma^{(1,2)}$ CI$^a$ |
| $2s^2p^2 \, ^1S_0$      | 21648 22140 22213 22335 21753$^b$ | 38 |
| $2s^2p^3 \, ^3S_2^o$    | 33735 33529 33234 33240 33498$^b$ | 146 |
| $2s^2p3s \, ^3P_0^o$    | 60333 59806 60182 60144 -47 |
| $2s^2p3s \, ^3P_1^o$    | 60353 59826 60202 60164 -24 |
| $2s^2p3s \, ^3P_2^o$    | 60393 59866 60243 60206 26 |
| $2s^2p3p \, ^1P_1^o$    | 61982 61587 61975 61911 62002$^b$ | 1 |
| $2s^2p^3 \, ^3D_3^o$    | 64087 64773 64628 64562 144 151(60) |
| $2s^2p^3 \, ^3D_1^o$    | 64090 64762 64617 64551 64036$^c$ | 137 141(60) |
| $2s^2p^3 \, ^3D_2^o$    | 64091 64766 64622 64555 140 145(60) |
| $2s^2p^3 \, ^3P_0^o$    | 75254 76209 76196 76153 117 111(60) |
| $2s^2p^3 \, ^3P_2^o$    | 75255 76214 76202 76158 121 |
| $2s^2p^3 \, ^3P_0^o$    | 75256 76207 76194 76151 115 |
| $2s^2p3d \, ^1D_2^o$    | 77680 79297 79724 79643 7 |
| $2s^2p4s \, ^3P_0^o$    | 78105 79737 80152 80076 -33 |
| $2s^2p4s \, ^3P_1^o$    | 78117 79750 80166 80090 -21 |
| $2s^2p4s \, ^3P_2^o$    | 78148 79787 80205 80130 24 |
| $2s^2p3d \, ^3F_2^o$    | 78199 79845 80271 80193 -31 |
| $2s^2p3d \, ^3F_3^o$    | 78216 79862 80289 80211 -18 |
| $2s^2p3d \, ^3D_1^o$    | 78293 79937 80354 80275 -13 |
| $2s^2p3d \, ^3D_2^o$    | 78308 79954 80371 80293 13 |
| $2s^2p3d \, ^3D_3^o$    | 78318 79966 80385 80306 29 |
| $2s^2p4s \, ^1P_1^o$    | 78340 79983 80403 80327 17 |
| $2s^2p3d \, ^1F_3^o$    | 78530 80802 80626 80549 15 |
| $2s^2p3d \, ^1P_1^o$    | 78731 80402 80822 80746 12 |
| $2s^2p3d \, ^3P_2^o$    | 79311 80957 81307 81225 18 |
| $2s^2p3d \, ^3P_1^o$    | 79319 80967 81318 81237 30 |
| $2s^2p3d \, ^3P_0^o$    | 79323 80972 81323 81242 35 |
| $2s^2p4d \, ^1D_2^o$    | 83498 86521 86942 86858 8 |

$^a$Berengut et al., 2004 [29]
$^b$Carlsson et al., 1995 [13]
$^c$Jönsson et al., 1996 [16]

within a few percent. In Table VI we compare our calculations with the few experiments that exist for carbon ions; in all cases agreement is within around 0.005 cm$^{-1}$, which corresponds to an error in $k_{SMS}$ of around 20 GHz·amu.

In Table VII we present total isotope shifts for some important transitions. These transitions can be observed in quasar absorption spectra, and can therefore be used to probe variation of $\alpha$ and isotope abundance evolution. The results are presented both in MHz and km/sec: the latter is the preferred form for use in astronomy.
TABLE V: Comparison of $k_{\text{SMS}}$ for transitions from the ground state in C1 using various methods. Note that the MCHF–CI results are non-relativistic and hence do not distinguish fine-structure.

| Level | Energy $k_{\text{SMS}}$ (GHz·amu) | 1s$^2$2p$^2$ 1S$^0_0$ | CI (expt.) | CI + Σ(1) | CI + Σ(1,2) | MCHF–CI |
|-------|---------------------------------|-----------------|----------|---------|---------|---------|
| 2s$^2$2p$^2$ 1S$^0_0$ | 21648 | 186 | 180 | 191 | 152$^a$ |
| 2s$^2$2p$^2$ 5S$^0_2$ | 33735 | -2540 | -2579 | -2588 | -2583$^a$ |
| 2s$^2$2p3s 3P$^0_0$ | 60333 | 1405 | 1405 | 1419 | 1420 |
| 2s$^2$2p3s 3P$^1_1$ | 60353 | 1406 | 1406 | 1420 | 1422 |
| 2s$^2$2p3s 3P$^2_2$ | 60393 | 1408 | 1408 | 1422 | 1422 |
| 2s$^2$2p3s 1P$^0_1$ | 61982 | 1549 | 1551 | 1559 | 1553$^a$ |
| 2s$^2$2p$^3$ 3D$^0_3$ | 64087 | -2165 | -2224 | -2227 | -2222$^b$ |
| 2s$^2$2p$^3$ 3D$^0_2$ | 64090 | -2165 | -2224 | -2227 | -2227 |
| 2s$^2$2p$^3$ 3P$^0_1$ | 75254 | -1272 | -1390 | -1392 | -1392 |
| 2s$^2$2p$^3$ 3P$^0_0$ | 75255 | -1272 | -1389 | -1391 | -1391 |
| 2s$^2$2p$^3$ 3P$^0_0$ | 75256 | -1271 | -1390 | -1392 | -1392 |
| 2s$^2$2p3d 1D$^0_2$ | 77680 | 1334 | 1320 | 1331 | 1331 |
| 2s$^2$2p4s 3P$^0_0$ | 78105 | 1398 | 1392 | 1407 | 1407 |
| 2s$^2$2p4s 3P$^1_1$ | 78117 | 1404 | 1397 | 1412 | 1412 |
| 2s$^2$2p4s 3P$^2_2$ | 78148 | 1415 | 1408 | 1422 | 1422 |
| 2s$^2$2p3d 3P$^0_0$ | 78199 | 1378 | 1368 | 1381 | 1381 |
| 2s$^2$2p3d 3F$^0_3$ | 78216 | 1381 | 1372 | 1384 | 1384 |
| 2s$^2$2p3d 3D$^0_3$ | 78293 | 1430 | 1422 | 1434 | 1434 |
| 2s$^2$2p3d 3D$^0_2$ | 78308 | 1429 | 1421 | 1432 | 1432 |
| 2s$^2$2p3d 3D$^0_3$ | 78318 | 1430 | 1420 | 1432 | 1432 |
| 2s$^2$2p4s 1P$^0_1$ | 78340 | 1443 | 1435 | 1446 | 1446 |
| 2s$^2$2p3d 1F$^0_3$ | 78530 | 1451 | 1440 | 1452 | 1452 |
| 2s$^2$2p3d 1P$^0_1$ | 78731 | 1436 | 1426 | 1438 | 1438 |
| 2s$^2$2p3d 3P$^0_0$ | 79311 | 948 | 998 | 1010 | 1010 |
| 2s$^2$2p3d 3P$^0_1$ | 79319 | 956 | 1006 | 1018 | 1018 |
| 2s$^2$2p3d 3P$^0_0$ | 79323 | 960 | 1009 | 1021 | 1021 |
| 2s$^2$2p4d 1D$^0_2$ | 83498 | 1277 | 1258 | 1268 | 1268 |

$a$Carlsson et al., 1995 $^{13}$
$b$Jönsson et al., 1995 $^{16}$

VI. ACKNOWLEDGEMENTS

This work is supported by the Australian Research Council; Department of Energy, Office of Nuclear Physics, Contract No. W-31-109-ENG-38; Gordon Godfrey fund; and Russian Foundation for Basic Research, grant No. 05-02-16914. The authors would like to thank V. A. Dzuba for useful discussions. We are grateful to the APAC National Facility for providing computer time.
TABLE VI: Comparison of calculated $^{13}\text{C} - ^{12}\text{C}$ isotope shifts with experiment.

| Transition          | $\lambda$ | $\delta\nu^{13,12}$ (cm$^{-1}$) | Expt. | This work |
|---------------------|-----------|---------------------------------|-------|-----------|
| C I                 | $2s^22p^2 \, ^3P_2$  | $2s^22p^3 \, ^5S^o_2$  | 2967  | 0.670(5)$^a$ | 0.674$^b$ |
|                     | $2s^22p^2 \, ^1S_0$  | $2s^22p3s \, ^1P^o_1$  | 2479  | -0.156(3)$^c$ | -0.151 -0.156(2)$^d$ |
| C II                | $2s^2p^2 \, ^2S_{1/2}$ | $2s^22p \, ^2P^o_3/2$  | 2837  | -0.612(2)$^c$ | -0.617 |
|                     | $2s^2p^2 \, ^2S_{1/2}$ | $2s^22p \, ^2P^o_1/2$  | 2838  | -0.623(3)$^c$ | -0.617 |

$^a$Bernheim and Kittrell, 1980
$^b$Actually, the $2s^22p^2 \, ^3P_0 - 2s^2p^3 \, ^5S^o_2$ transition was calculated.
$^c$Burnett, 1950
$^d$Holmes, 1951

TABLE VII: Total $^{13}\text{C} - ^{12}\text{C}$ and $^{14}\text{C} - ^{12}\text{C}$ isotope shifts for important transitions. We believe the errors are of the order of 0.1 GHz.

| Transition          | $\lambda$ | $\delta\nu^{13,12}$ (GHz) | $\delta\nu^{14,12}$ (GHz) |
|---------------------|-----------|--------------------------|--------------------------|
| Ground State Upper Level (Å) | (GHz) | (km/sec)$^a$ | (GHz) | (km/sec)$^a$ |
| C I                 | $2s^22p^2 \, ^3P_0$  | 1657  | -2.75 | 0.46 | -5.09 | 0.84 |
|                     | $2s^22p^3 \, ^3P^o_1$  | 1560  | 21.10 | -3.29 | 39.12 | -6.10 |
|                     | $2s^22p^3 \, ^3P^o_2$  | 1329  | 16.91 | -2.25 | 31.34 | -4.17 |
|                     | $2s^22p4s \, ^3P^o_1$  | 1280  | -0.82 | 0.10 | -1.51 | 0.19 |
|                     | $2s^22p3d \, ^3D^o_1$  | 1277  | -0.94 | 0.12 | -1.75 | 0.22 |
|                     | $2s^22p4s \, ^1P^o_1$  | 1276  | -1.01 | 0.13 | -1.88 | 0.24 |
|                     | $2s^22p3d \, ^3P^o_1$  | 1261  | 1.84 | -0.23 | 3.42 | -0.43 |
| C II                | $2s^2p^2 \, ^2P^o_1/2$  | 1336  | 25.10 | -3.35 | 46.53 | -6.21 |
|                     | $2s^2p^2 \, ^2D_{3/2}$  | 1336  | 25.10 | -3.35 | 46.54 | -6.21 |
|                     | $2s^2p^2 \, ^2D_{5/2}$  | 1336  | 25.10 | -3.35 | 46.54 | -6.21 |
|                     | $2s^2p^2 \, ^2S_{1/2}$  | 1037  | 18.70 | -1.94 | 34.66 | -3.59 |
| C III               | $2s^2 \, ^1S_0$  | 2s$^2p \, ^1P^o_1$  | 977  | 28.76 | -2.81 | 53.33 | -5.21 |
| C IV                | $2s \, ^2S_{1/2}$  | $2p \, ^2P^o_1/2$  | 1551  | 35.89 | -5.57 | 66.54 | -10.32 |
|                     | $2p \, ^2P^o_3/2$  | 1548  | 35.79 | -5.54 | 66.35 | -10.27 |

$^a\delta\nu = \delta\lambda/\lambda \times c$ (km/sec). A negative velocity means that $^{14}\text{C}$ (and $^{13}\text{C}$) are at lower wavelength than $^{12}\text{C}$.
APPENDIX A: MATRIX ELEMENT OF THE TWO-BODY OPERATOR

The two-body operator used in this work is the sum of the Coulomb interaction operator and the “rescaled” SMS operator (atomic units):

\[
\tilde{Q} = \frac{1}{|r_1 - r_2|} + \lambda \mathbf{p}_1 \cdot \mathbf{p}_2 \equiv \sum_k \tilde{Q}_k, \quad (A1)
\]

where \(\lambda\) is the scaling factor, \(\mathbf{p} = -i\nabla\) is electron momentum, and

\[
\tilde{Q}_k = \frac{4\pi}{2k + 1} \frac{r^k}{r_k^{k+1}} Y_k(n_1)Y_k(n_2) + \lambda \mathbf{p}_1 \cdot \mathbf{p}_2 \delta_{k1}. \quad (A2)
\]

We use the following form for the single-electron wave function

\[
\phi(r)_{jlm} = \frac{1}{r} \left( \frac{f(r)\Omega(n)_{jlm}}{i\alpha g(r)\Omega(n)_{jlm}} \right). \quad (A3)
\]

Here \(\alpha = 1/137.036\) is the fine structure constant, and \(\tilde{\Omega}(n)_{jlm} = -(\vec{\sigma} \cdot \mathbf{n})\Omega(n)_{jlm}\).

The matrix element of operator (A2) with wave functions (A3) has the form

\[
\langle \phi_a(r_1)\phi_b(r_2) | \tilde{Q}_k | \phi_c(r_1)\phi_d(r_2) \rangle = C_{ab,cd}^k (R_{ab,cd}^k - \lambda \delta_{k1} p_{ac} p_{bd}), \quad (A4)
\]

where the angular factor \(C_k\) is the same for both operators

\[
C_{ab,cd}^k = (-1)^{q+m_a+m_b} \left( \begin{array}{ccc} j_a & k & j_c \\ -m_a & q & m_c \end{array} \right) \left( \begin{array}{ccc} j_b & k & j_d \\ -m_b & -q & m_d \end{array} \right) \\
\times (-1)^{j_a+j_b+j_c+j_d+1} \sqrt{(2j_a+1)(2j_b+1)(2j_c+1)(2j_d+1)} \\
\times \left( \begin{array}{ccc} j_a & j_c & k \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{array} \right) \left( \begin{array}{ccc} j_b & j_d & k \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{array} \right) \xi(l_a + l_c + k)\xi(l_b + l_d + k), \quad (A5)
\]

\[
\xi(x) = \begin{cases} 1, & \text{if } x \text{ is even} \\ 0, & \text{if } x \text{ is odd} \end{cases}
\]

\(R_{ab,cd}^k\) is radial Coulomb integral

\[
R_{ab,cd}^k = \int_0^{\infty} \frac{r^k}{r_k^{k+1}} \left( f_a(r_1)f_c(r_1) + \alpha^2 g_a(r_1)g_c(r_1) \right) \left( f_b(r_2)f_d(r_2) + \alpha^2 g_b(r_2)g_d(r_2) \right) dr_1 dr_2, \quad (A6)
\]

while \(p_{12}\) is the radial matrix element of the SMS operator

\[
p_{12} = A_{12}\delta_{l_1l_2+1} + B_{12}\delta_{l_1l_2-1}, \quad (A7)
\]

\[
A_{12} = \int_0^{\infty} f_1 \left( \frac{d}{dr} - \frac{l_1}{r} \right) f_2 dr, \quad B_{12} = \int_0^{\infty} f_1 \left( \frac{d}{dr} + \frac{l_2}{r} \right) f_2 dr.
\]
APPENDIX B: EFFECTIVE INTEGRALS FOR \( \Sigma \) DIAGRAMS

Here we give expressions for the diagrams in Figs. 1-4. The following conventions for the indices are used: \( a, b, c, \) and \( d \) correspond to the external lines (valence electrons); \( 1 \leq m, n \leq N_{\text{core}}; \) \( N_{\text{core}} + 1 \leq \alpha, \beta. \) Following [22] we use the shorthand notation \([j,k,\ldots]\) = \((2j+1)(2k+1)\ldots.\) Note also that all Wigner three–j symbols come with a parity selection rule, which is not explicitly given. This is because the three–j terms come from the formula

\[
-\left[ l_1, l_2 \right]^{1/2} \left( \begin{array}{ccc} l_1 & k & l_2 \\ 0 & 0 & 0 \end{array} \right) \left( \begin{array}{ccc} j_1 & j_2 & k \\ l_1 & l_2 & \end{array} \right) = \left( \begin{array}{ccc} j_1 & j_2 & k \\ 1/2 & -1/2 & 0 \end{array} \right) \xi(l_1 + l_2 + k).
\]

Additionally, the subtraction diagrams (Figs. 2 and 4) have terms which are matrix elements of \( h_{\text{CI}} \) (see Eq. (14)). This operator cannot change the angular momentum of the state; for example \( \langle a| h_{\text{CI}} |n \rangle \) comes with a factor \( \delta_{ja,jb}, \delta_{ma,mb}, \) and \( \delta_{la,lb}. \)

We start with the contributions to the self-energy matrix elements from the diagrams of Figs. 1 and 2. All of these expressions have the following additional terms that we do not write explicitly: \( \delta_{ja,jb}, \delta_{ma,mb}, \) and \( \delta_{la,lb}.

Fig. 1.1:

\[
D_{a,b} = \sum_{\substack{\alpha,\beta \\k}} \frac{|j_n, j_a, j_\beta|}{|k|} \left( \begin{array}{ccc} j_a & j_\beta & k \\ 1/2 & -1/2 & 0 \end{array} \right) \left( \begin{array}{ccc} j_n & j_\alpha & k \\ 1/2 & -1/2 & 0 \end{array} \right) \frac{R_{an,\beta a}^k R_{\beta a,\alpha n}^k}{\epsilon_a + \epsilon_n - \epsilon_\alpha - \epsilon_\beta}
\]

(B1)

Fig. 1.2:

\[
D_{a,b} = \sum_{\substack{\alpha,\beta \\k}} (-1)^{j_a} [j_n, j_a, j_\beta] \left( \begin{array}{ccc} j_a & j_\beta & k_1 \\ 1/2 & -1/2 & 0 \end{array} \right) \left( \begin{array}{ccc} j_n & j_\alpha & k_1 \\ 1/2 & -1/2 & 0 \end{array} \right) \frac{R_{an,\beta a}^k R_{\beta a,\alpha n}^k}{\epsilon_a + \epsilon_n - \epsilon_\alpha - \epsilon_\beta}
\]

\times \left( \begin{array}{ccc} j_a & j_\beta & k_2 \\ 1/2 & -1/2 & 0 \end{array} \right) \left( \begin{array}{ccc} j_n & j_\alpha & k_2 \\ 1/2 & -1/2 & 0 \end{array} \right) \frac{R_{an,\beta a}^k R_{\beta a,\alpha n}^k}{\epsilon_a + \epsilon_n - \epsilon_\alpha - \epsilon_\beta}
\]

(B2)

Fig. 1.3:

\[
D_{a,b} = -\sum_{\substack{\alpha,\beta \\k}} [j_m, j_n, j_\alpha] \left( \begin{array}{ccc} j_a & j_m & k \\ 1/2 & -1/2 & 0 \end{array} \right) \left( \begin{array}{ccc} j_n & j_\alpha & k \\ 1/2 & -1/2 & 0 \end{array} \right) \frac{R_{aa,\alpha m}^k R_{mn,\alpha a}^k}{\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta}
\]

(B3)

Fig. 1.4:

\[
D_{a,b} = \sum_{\substack{\alpha,\beta \\k}} (-1)^{k_1+2k_2+1} [j_n, j_m, j_\alpha] \left( \begin{array}{ccc} j_a & j_m & k_1 \\ 1/2 & -1/2 & 0 \end{array} \right) \left( \begin{array}{ccc} j_n & j_\alpha & k_1 \\ 1/2 & -1/2 & 0 \end{array} \right) \frac{R_{aa,\alpha m}^k R_{mn,\alpha a}^k}{\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta}
\]

\times \left( \begin{array}{ccc} j_n & j_a & k_2 \\ 1/2 & -1/2 & 0 \end{array} \right) \left( \begin{array}{ccc} j_m & j_\alpha & k_2 \\ 1/2 & -1/2 & 0 \end{array} \right) \frac{R_{aa,\alpha m}^k R_{mn,\alpha a}^k}{\epsilon_m + \epsilon_n - \epsilon_\alpha - \epsilon_\beta}
\]

(B4)

Fig. 2.1:

\[
D_{a,b} = \sum_{\alpha} |j_n| \frac{R_{an,\beta a}^0 \langle n| h_{\text{CI}} |\alpha \rangle}{\epsilon_n - \epsilon_\alpha}
\]

(B5)

Fig. 2.2:

\[
D_{a,b} = \sum_{\alpha} (-1)^{j_a} |j_n| \frac{R_{aa,\alpha m}^k \langle n| h_{\text{CI}} |\alpha \rangle}{\epsilon_n - \epsilon_\alpha}
\]

(B6)
Next we present contributions to the valence-valence screening diagrams due to the diagrams of Figs. 3 and 4. These diagrams have $k$ as an external parameter (not to be summed over). In the CI procedure they are added to $R_{ab,cd}^k$ of Eq. (A4).

Fig. 3.1:

$$R_{ab,cd}^k = \sum_{na} [j_n, j_n] [k] \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \sum_{\alpha \beta} \frac{\langle a | h^{CI} | n \rangle \langle n | h^{CI} | b \rangle}{\epsilon_n - \epsilon_\alpha}$$

Fig. 3.2:

$$R_{ab,cd}^k = \sum_{na} (-1)^{k_1 + k} [j_\alpha, j_n] \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \sum_{\alpha \beta} \frac{\langle a | h^{CI} | n \rangle \langle n | h^{CI} | b \rangle}{\epsilon_n - \epsilon_\alpha}$$

Fig. 3.3:

$$R_{ab,cd}^k = \sum_{na} (-1)^{k_1 + k} [j_\alpha, j_n] \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \sum_{\alpha \beta} \frac{\langle a | h^{CI} | n \rangle \langle n | h^{CI} | b \rangle}{\epsilon_n - \epsilon_\alpha}$$

Fig. 3.4:

$$R_{ab,cd}^k = \sum_{na} (-1)^{j_\alpha + j_n + j_\alpha + j_n} [j_\alpha, j_n] \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \left( j_\alpha j_n \right) \sum_{\alpha \beta} \frac{\langle a | h^{CI} | n \rangle \langle n | h^{CI} | b \rangle}{\epsilon_n - \epsilon_\alpha}$$

Fig. 3.5:
\[ R_{ab,cd}^k = \sum_{mn}^{k_1 k_2} (-1)^{j_a + j_b + j_c + j_d + j_m + j_n + k_1 + k_2 + 1} [j_m, j_n, k] \left( \begin{array}{c} j_a \\ j_m \\ k_1 \\ j_b \\ j_n \\ k_1 \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array} \right) \left( \begin{array}{c} j_a \\ j_c \\ k_2 \\ j_d \\ j_m \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array} \right) \left( \begin{array}{c} j_b \\ j_d \\ k \end{array} \right) \right)^{-1} \times \left( \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array} \right) \left( \begin{array}{c} \frac{1}{2} \\ -\frac{1}{2} \end{array} \right) \times \left\{ \begin{array}{c} j_c \\ j_a \\ k_1 \\ k_2 \\ j_m \end{array} \right\} \left\{ \begin{array}{c} j_d \\ j_b \\ k_1 \\ k_2 \\ j_n \end{array} \right\} \frac{R_{kn,cd}^{k_1} R_{mn}^{k_2}}{\epsilon_m + \epsilon_n - \epsilon_c - \epsilon_d} \right) \] (B13)

Fig. 4.1:

\[ R_{ab,cd}^k = -\sum_n R_{nb,cd}^{k} \langle a | h_{CI} | n \rangle \frac{1}{\epsilon_n - \epsilon_a} \] (B14)

Fig. 4.2:

\[ R_{ab,cd}^k = -\sum_n R_{an,cd}^{k} \langle b | h_{CI} | n \rangle \frac{1}{\epsilon_n - \epsilon_b} \] (B15)

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