Do theory and experiment agree for the nuclear shielding difference between alkali atoms and ions in magnetic resonance?

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Abstract. For each alkali metal (M) in the gas phase, the difference $\Delta\sigma(M)$ between the nuclear shielding of the neutral atom and of the first positive ion is computed from non-relativistic Hartree-Fock theory. The contributions to $\Delta\sigma(M)$ arising from electron correlation are derived from the Hellmann-Feynman theorem by combining Dirac-Fock and experimental ionisation potentials and are shown to be small. It is also shown that $\Delta\sigma(M)$ must be positive in contrast to the reported experimental result for $\Delta\sigma(Cs)$.

   The results of the present theory agree with experiment for $\Delta\sigma(Rb)$ and two previous methods for calculating $\Delta\sigma(M)$ are shown to be completely untrustworthy. The reported experimental value for $\Delta\sigma(K)$ is seven times larger than the present theoretical result whilst that reported experimentally for $\Delta\sigma(Cs)$ is not even positive. It is concluded that the discrepancies between theory and experiment for both $\Delta\sigma(K)$ and $\Delta\sigma(Cs)$ greatly exceed any errors in the present calculations, and hence that the experimental values should be re-examined.

1. Introduction

In nuclear magnetic resonance experiments, the frequency of the electromagnetic radiation needed to induce transitions of the nuclear spins between their energy levels in a static external magnetic field depends upon the electronic environment of the nucleus. This dependence arises because the motion of the electrons caused by the external field ($\boldsymbol{B}_0$) creates an additional magnetic field at the nucleus which therefore experiences a field ($\boldsymbol{B}'$) different from $\boldsymbol{B}_0$. The difference between the $\boldsymbol{B}'$ field and the applied field $\boldsymbol{B}_0$ defines the magnetic shielding tensor $\boldsymbol{\sigma}$ (Abragam 1961) through

$$\boldsymbol{B}' = \boldsymbol{B}_0 - \boldsymbol{\sigma} : \boldsymbol{B}_0. \tag{1}$$

It is important that the theory of nuclear shielding be thoroughly understood because magnetic resonance methods are extensively used throughout physics and chemistry.

   The most direct method of testing the standard non-relativistic theory of nuclear shielding (Ramsey 1950) would be to derive $\boldsymbol{\sigma}$ by comparing the results of a resonance experiment on a bare nucleus with one in which the nucleus is embedded in an atom or a molecule. However such a test has not yet been carried out because it has not been possible to perform accurate experiments on bare nuclei. Nevertheless the difference $(\sigma_l(H_2O) - \sigma(H))$ between the trace $(\sigma_l(H_2O))$ of the proton shielding tensor in liquid water and the shielding $(\sigma(H))$ of the hydrogen atom is known from experiment

to be 7.91 ppm (Winkler *et al* 1972) by combining a measurement of the electron: proton
g-factor ratio (Winkler *et al* 1972) with one of the electron: water g-factor ratio (Lambe
1969). The difference between the proton shielding in liquid water and the hydrogen
molecule has also been measured to be -0.63 ppm (Thomas 1950, Hardy 1959) yielding
an experimental value for $\sigma(H_2) - \sigma(H)$ of 8.54 ppm. The shielding for the hydrogen
atom can be calculated exactly ($=17.73$ ppm, Winkler *et al* 1972) whilst that for the
hydrogen molecule is computed to be 26.20 ppm using coupled Hartree-Fock theory
plus vibrational averaging (Ditchfield 1981) and 27.56 ppm using a correlated wavefunc-
tion (Ishiguro and Koide 1954) without vibrational averaging. The agreement between
the theoretical (8.47 ppm by coupled Hartree-Fock theory and 9.83 ppm for the
correlated wavefunction) and experimental (8.54 ppm) values of $\sigma(H_2) - \sigma(H)$ provides
strong evidence that the Ramsey theory (Ramsey 1950) is correct. The recent coupled
Hartree-Fock result (Ditchfield 1981) is probably more reliable than the older corre-
lated one because there is evidence (Sadlej and Raynes 1978, Daborn and Handy 1981)
that electron correlation makes only a small contribution to the shielding. A second
value for $\sigma(H_2)$ is calculated by adding the paramagnetic contribution (Ramsey 1950)
of -5.725 ppm, derived from the experimental spin-rotation interaction constant (Reid
1975), to the diamagnetic contribution (Lamb 1941, Ramsey 1950) of 32.02 ppm,
computed from a highly accurate correlated wavefunction for the H_2 ground state
(Reid 1975). The close agreement between the resulting prediction of 8.56 ppm for
$\sigma(H_2) - \sigma(H)$ with the experimental value of 8.54 ppm provides further strong evidence
that the Ramsey theory is correct. An experimental value for the difference $\sigma(H_2O) -$
$\sigma(H)$ between the shielding in gaseous H_2O and that in the hydrogen atom is derived
by combining the measurements $\sigma(H_2O)$ (gas) $= 30.052$ ppm and $\sigma_l(H_2O)$ (liquid at
25 °C) $= 25.688$ ppm (Raynes 1978) with the value of 7.91 ppm for $\sigma_l(H_2O) - \sigma(H)$
(Winkler *et al* 1972). The resulting experimental value of 12.27 ppm for $\sigma(H_2O) - \sigma(H)$
agrees well with the theoretical prediction of 12.40 ppm calculated by subtracting
17.73 ppm ($\sigma(H)$) from the coupled Hartree-Fock result for $\sigma(H_2O)$ of 30.13 ppm
(Holler and Lischka 1980).

Although there is a vast literature of calculations of nuclear shielding (e.g. Jameson
1982), the three-proton shieldings discussed seem to be the only ones for which reliable
theoretical and experimental data are simultaneously available. Nevertheless it should
be pointed out that, with the two exceptions discussed in this paper, no calculations
of nuclear shielding have shown discrepancies with experiment which could not be
plausibly ascribed to approximations made in describing the electronic structure of
the species.

The evidence outlined above causes it to be widely, and almost certainly correctly,
believed that the non-relativistic theory (Ramsey 1950) of nuclear shielding is correct.
However very serious discrepancies between theory and experiment have been reported
(Davis *et al* 1974, Oluwole 1977, Obiajunwa *et al* 1983) for the difference ($\Delta\sigma(M) =$
$\sigma(M) - \sigma(M^+)$) between the shieldings ($\sigma(M)$) in three gaseous alkali atoms and those
($\sigma(M^+)$) in their gaseous first positive ions. This paper has two main objectives. The
first is to point out that the values of $\Delta\sigma(M)$ for both Rb and Cs calculated previously
(Davis *et al* 1974, Oluwole 1977) use theories which are so poor that the results cannot
be credited with any significance. It is then shown that for Rb a reliable calculation
using Hartree-Fock theory brings theory and experiment into agreement. The second
object of this paper is to show that the correlation contribution to $\Delta\sigma(M)$ is far too
small to explain the large discrepancies between theory and experiment which remain
for both K and Cs; this means that the experimental values are probably in error and

should be re-examined. An additional argument is given to show that the shielding in each neutral metal is greater than that in its first positive ion which shows that the experimental result (Oluwole 1977) that gives $\Delta\sigma(\text{Cs}) < 0$ is incorrect.

Both the presentation of accurate predictions of $\Delta\sigma(\text{M})$ for all the alkalis and the development of methods for reliably deriving the correlation contribution to these differences constitute two useful byproducts of this work. The use of similar calculations in the interpretation of NMR spectra of alkali anions in solution will be reported elsewhere.

2. Predictions of nuclear shieldings

2.1. Hartree-Fock shieldings

In the Ramsey theory the total shielding is the sum of a diamagnetic and a paramagnetic part. In non-relativistic theory using exact electronic wavefunctions the paramagnetic shielding vanishes for any atomic S state, whether closed or open shell (Hylleraas and Skavlem 1950), if the origin defining the vector potential of the B_0 field is taken at the centre of the nuclear charge distribution which is taken to be spherical. The trace $\sigma_{\text{ex}}(\text{G})$ of the diamagnetic part of the exact shielding tensor for an S state of species G is then defined through the exact N-electron wavefunction $|\psi_{\text{exG}}(r_1 \ldots r_N)\rangle$ for G by

$$\sigma_{\text{ex}}(\text{G}) = \left\langle \psi_{\text{exG}}(r_1 \ldots r_N) \middle| \sum_{i=1}^{N} r_i^2 A_{\text{rn}}(r_i) \middle| \psi_{\text{exG}}(r_1 \ldots r_N) \right\rangle (3c^2)^{-1}. \tag{2}$$

Here c is the velocity of light in atomic units and the purely radial function $A_{\text{rn}}(r)$ defines the vector potential $\hat{A}_{\text{rn}}(r)$ generated by the nuclear magnetisation through

$$\hat{A}_{\text{rn}}(r) = \gamma_n \hat{I}_n \times r A_{\text{rn}}(r) c^{-2} \tag{3}$$

where γ_n is the nuclear gyromagnetic ratio and $\hat{I}_n$ is the nuclear spin operator. In the point dipole description of the nuclear magnetisation $A_{\text{rn}}(r)$ is r^{-3}, whilst for the model in which the magnetisation is uniformly distributed over the surface of a sphere of radius r_n, $A_{\text{rn}}(r)$ equals r^{-3} for $r \geq r_n$ but equals r_n^{-3} for $r \leq r_n$ (Lindgren and Rosen 1974).

If the electronic wavefunction in the exact expression (2) is approximated by the Hartree-Fock function, the shieldings for a neutral alkali atom ($\sigma_{\text{HF}}(\text{M})$) and its first positive ion ($\sigma_{\text{HF}}(\text{M}^+)$) are given by the orbital sums

$$\sigma_{\text{HF}}(\text{M}) = \left[2 \left(\sum_C \langle C(\text{M})|r^2 A_{\text{rn}}(r)| C(\text{M})\rangle \right) + \langle V(\text{M})|r^2 A_{\text{rn}}(r)| V(\text{M})\rangle \right] (3c^2)^{-1} \tag{4a}$$

$$\sigma_{\text{HF}}(\text{M}^+) = 2 \sum_C \langle C(\text{M}^+)|r^2 A_{\text{rn}}(r)| C(\text{M}^+)\rangle (3c^2)^{-1}. \tag{4b}$$

Here $C(\text{M})$ and $C(\text{M}^+)$ are the purely spatial Hartree-Fock core orbitals of the neutral and the first positive ion of M and $V(\text{M})$ is the spatial valence Hartree-Fock s orbital of the neutral atom. The factors of two arise because each core orbital contains two electrons. The Hartree-Fock prediction ($\Delta\sigma_{\text{HF}}(\text{M})$) of the shielding difference derived from (4) decomposes into a sum of a core ($\Delta\sigma_{\text{HFC}}(\text{M})$) and a valence ($\sigma_{\text{HFV}}(\text{M})$) contribution

$$\Delta\sigma_{\text{HF}}(\text{M}) = \Delta\sigma_{\text{HFC}}(\text{M}) + \sigma_{\text{HFV}}(\text{M}) \tag{5a}$$

$$\Delta\sigma_{\text{HFC}}(\text{M}) = 2 \sum_C (\langle C(\text{M})|r^2 A_{\text{rn}}(r)| C(\text{M})\rangle - \langle C(\text{M}^+)|r^2 A_{\text{rn}}(r)| C(\text{M}^+)\rangle)(3c^2)^{-1} \tag{5b}$$

$$\sigma_{HFV}(M) = \langle V(M)|r^2 A_{rn}(r)|V(M)\rangle (3c^2)^{-1}. \qquad (5c)$$

The non-relativistic orbitals required in (4), which were taken to satisfy the usual symmetry and equivalence restrictions (Nesbet 1955), were computed by running the Oxford Dirac-Fock programme (Grant *et al* 1980) with an artificially large value of the velocity of light. For atomic S states this procedure reproduces exactly the results of conventional non-relativistic calculations (Wood and Pyper 1980).

The Hartree-Fock shieldings and shielding differences predicted using the point-charge point-dipole (i.e. $A_{rn}(r) = r^{-3}$) description of the nucleus are compared with the reported experimental values of $\Delta\sigma(M)$ in table 1. The shieldings $\sigma_{HF}(M)$ and $\sigma_{HF}(M^+)$ predicted when the nuclear charge is described as uniformly distributed throughout a sphere of radius r_n with the nuclear magnetisation residing on the surface are less than 0.05 ppm smaller than those of table 1 except for $\sigma_{HF}(Cs)$ and $\sigma_{HF}(Cs^+)$ which are 0.21 ppm smaller; all the $\Delta\sigma_{HF}(M)$ predictions being identical to those of table 1 to within 10^{-4} ppm. The results also show that, although the total shieldings are dominated by the contributions from the core orbitals, the core makes only a small contribution ($\Delta\sigma_{HFC}(M)$) to $\Delta\sigma_{HF}(M)$ because the neutral ($C(M)$) and ion ($C(M^+)$) core orbitals are very similar. The core contributes negatively to $\Delta\sigma_{HF}(M)$ because removal of the valence electron slightly reduces the electron density in the core region thereby allowing the core orbitals to contract slightly.

Table 1. Hartree-Fock shieldings for alkali atoms and cations (ppm†).

	$\sigma_{HF}(M^+)$	$\sigma_{HF}(M)$	$\Delta\sigma_{HF}(M)$	$\Delta\sigma_{expt}(M)$‡	$\Delta\sigma_{HFC}(M)$
Li	95.404	101.450	6.046		−0.085
Na	623.805	628.894	5.089		−0.261
K	1325.421	1329.354	3.933	29 ± 6	−0.267
Rb	3363.200	3366.793	3.593	3.8 ± 2.6	−0.272
Cs	5777.031	5780.199	3.169	-7.1 ± 2.0	−0.243

† For definitions, see text.
‡ Experiment: Obiajunwa *et al* (1983) (K), Davis *et al* (1974) (Rb), Oluwole 1977 (Cs).

The results of table 1 show that there is agreement between the theoretical and experimental shielding difference for Rb ($\Delta\sigma(Rb)$). This shows that for Rb the discrepancies between theory and experiment reported previously (Davis *et al* 1974) originated solely from inadequate theory. The previous theoretical value of -8.2 ppm for $\Delta\sigma(Rb^+)$ (Davis *et al* 1974), which even has the wrong sign, was derived by subtracting the values of $\sigma(Rb)$ and $\sigma(Rb^+)$ predicted by a simple three-parameter formula (Malli and Fraga 1966) constructed to reproduce the Hartree-Fock shieldings of lighter systems. Although the three-parameter formula can reproduce the large total shieldings to within approximately 1%, it could never have been intended for the calculation of the much smaller shielding differences of interest here. Clearly independent errors of 1% in the predictions of $\sigma(M)$ and $\sigma(M^+)$ can give a value of $\Delta\sigma(M)$ that is entirely meaningless. The second previous theoretical prediction for $\Delta\sigma(Rb)$ of 140 ppm is reported (Davis *et al* 1974) as having been calculated from the formula (Lamb 1941)

$$\sigma(G) = 31.9(Z_G)^{4/3} \text{ ppm} \qquad (6)$$

derived by using the Thomas-Fermi description of a neutral atom. Since the calculation of $\Delta\sigma(\mathrm{M})$ requires the shielding $(\sigma(\mathrm{M}^+))$ for M^+, which is not a neutral system, (6) is not applicable directly. However $\sigma(\mathrm{M}^+)$ was calculated from (6) by equating $\sigma(\mathrm{M}^+)$ to the shielding produced by the isoelectronic inert gas. This approximation is very poor and thus gives a meaningless value for $\Delta\sigma(\mathrm{M})$. Indeed the quantity $\sigma_{\mathrm{HF}}(\mathrm{Rb}) - \sigma_{\mathrm{HF}}(\mathrm{Kr}) = 121$ ppm bears no resemblance to the Hartree-Fock prediction $(\Delta\sigma_{\mathrm{HF}}(\mathrm{Rb}))$ of table 1. Similar calculations for K and Cs again give meaningless values of 112 ppm and 161 ppm† respectively for $\Delta\sigma(\mathrm{M})$. It is also found that differencing the neutral and cation shieldings predicted from the three-parameter formula of Malli and Fraga (1966) yields an unrealistic value of 89 ppm for $\Delta\sigma(\mathrm{Cs})$. (The value of 179 ppm reported by Oluwole (1977) appears to be in error). For both K and Cs, table 1 shows that the disagreement between Hartree-Fock theory and experiment is very marked. The Hartree-Fock prediction of $\Delta\sigma(\mathrm{K})$, which agrees as expected with previous calculations (Dickinson 1950), is only one seventh of the reported experimental value (Obiajunwa *et al* 1983) whilst the negative sign of the reported experimental value of $\Delta\sigma(\mathrm{Cs})$ (Oluwole 1977) is most surprising.

2.2. Electron correlation corrections

It is now shown that electron correlation makes only a small contribution to the shielding difference $\Delta\sigma(\mathrm{M})$ and hence that the large discrepancies between the experimental and Hartree-Fock predictions of $\Delta\sigma(\mathrm{M})$ for K and Cs do not arise from correlation. The core-valence correlation contributes positively to $\sigma(\mathrm{M})$ and hence to $\Delta\sigma(\mathrm{M})$ because the introduction of correlation to the Hartree-Fock function reduces the core-valence repulsion thereby allowing the valence orbital to contract (Partridge *et al* 1983). This shows that core-valence correlation cannot be responsible for the discrepancy in Cs for which a negative experimental $\Delta\sigma(\mathrm{M})$ value is reported (Oluwole 1977). Although the core-valence correlation will increase $\Delta\sigma(\mathrm{K})$, it is contrary to all evidence from previous calculations to suppose that this could be six times as large as $\Delta\sigma_{\mathrm{HF}}(\mathrm{K})$ as would be required to explain the discrepancy between theory and experiment. Thus correlation only increases the first ionisation potentials of alkali metals by approximately 10% and reduces a suitably defined mean radius of the valence orbital by 3% (Partridge *et al* 1983). Only the core-core correlation contribution to $\Delta\sigma(\mathrm{M})$, whose sign is not known with certainty, might in principle be responsible for the discrepancy for Cs. However, the close similarity between the core orbitals of Cs and those of Cs^+ as manifested by the small core contribution $(\Delta\sigma_{\mathrm{HFC}}(\mathrm{Cs}) = -0.24$ ppm) coupled with the result (Partridge *et al* 1983) that core-core correlation scarcely changes $\langle r^2 \rangle$ for Cs means that the core-core correlation contribution to $\Delta\sigma(\mathrm{Cs})$ is highly unlikely to be 50 times larger than $\Delta\sigma_{\mathrm{HFC}}(\mathrm{Cs}^+)$. This core-core correlation contribution would have to have this magnitude to explain the Cs discrepancy.

The conclusion that correlation makes only a small contribution to $\Delta\sigma(\mathrm{M})$ and cannot therefore be responsible for the discrepancies between theory and experiment can be justified more quantitatively by invoking the Hellmann-Feynman theorem. This theorem is obeyed not only by the exact neutral and cation wavefunctions (Feynman 1939) but also by the closed-shell Hartree-Fock cation wavefunctions and by the restricted open-shell Hartree-Fock functions of the neutral alkalis (Epstein 1974). The

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† The value of -170 ppm reported as the result of such a calculation for Cs (Oluwole 1977) appears to be in error.

exact and Hartree–Fock energies of the system having nuclear charge Z and isoelectronic with the species G, where G = alkali atom M or cation M^+, will be denoted by $E_{\mathrm{exG}}(Z)$ and $E_{\mathrm{HFG}}(Z)$ respectively. Differentiation of these energies with respect to Z yields (Mazziotti 1970, Mehrotra and Saxena 1975) an expression for the contribution, arising from electron correlation, $\sigma_{\mathrm{corr}}(G)$ to the nuclear shielding in species G, i.e.

$$\sigma_{\mathrm{corr}}(G) = \sigma_{\mathrm{ex}}(G) - \sigma_{\mathrm{HF}}(G) = -\frac{1}{3c^2}\frac{\mathrm{d}}{\mathrm{d}Z}(E_{\mathrm{exG}}(Z) - E_{\mathrm{HFG}}(Z))_{Z=Z_{\mathrm{M}}}. \tag{7}$$

Here $(E_{\mathrm{exG}}(Z) - E_{\mathrm{HFG}}(Z))$ is the correlation energy of the species isoelectronic with G and having nuclear charge Z, and Z_{M} is the nuclear charge of the alkali metal M. For two- and three-electron atoms, the derivatives of the correlation energy with respect to Z entering (7) can be evaluated because the correlation energies are known accurately from both experiment (Clementi 1963) and *ab initio* calculation (Frankowski and Pekeris 1966). For the heavier alkalis $\sigma_{\mathrm{corr}}(M)$ and $\sigma_{\mathrm{corr}}(M^+)$ cannot be evaluated from (7) in practice because neither the total correlation energies nor their nuclear charge dependences are currently available. However an expression for the correlation contribution $\Delta\sigma_{\mathrm{corr}}(M)$ to the neutral–cation shielding difference $\Delta\sigma(M)$ can be derived by subtracting the result (7) for $\sigma_{\mathrm{corr}}(M^+)$ from the corresponding result for $\sigma_{\mathrm{corr}}(M)$. Thus

$$\Delta\sigma_{\mathrm{corr}}(M) = \frac{1}{3c^2}\left(\frac{\mathrm{d}I_{\mathrm{corrM}}(Z)}{\mathrm{d}Z}\right)_{Z=Z_{\mathrm{M}}} \tag{8}$$

with

$$I_{\mathrm{corrM}}(Z) = (E_{\mathrm{exM^+}}(Z) - E_{\mathrm{exM}}(Z)) - (E_{\mathrm{HFM^+}}(Z) - E_{\mathrm{HFM}}(Z)). \tag{9}$$

Here $I_{\mathrm{corrM}}(Z)$ is the contribution, arising from electron correlation, to the ionisation potential $I_{\mathrm{M}}(Z)$ for the removal of the valence s electron from the system of nuclear charge Z and isoelectronic with the neutral alkali M. The result (8) is useful because the Z dependence of $I_{\mathrm{corrM}}(Z)$ can be derived from experimental ionisation potentials. A linear approximation to $(\mathrm{d}I_{\mathrm{corrM}}(Z)/\mathrm{d}Z)_{Z=Z_{\mathrm{M}}}$ can be derived from the correlation contributions to the first ionisation potentials of the alkali metals and the second ionisation potentials of the alkaline earths. Quadratic and cubic approximations can be derived by also making use of the third ionisation potentials of the group IIIA elements and the fourth ionisation potentials of the group IVA elements. Each quantity $I_{\mathrm{corrM}}(Z)$ is derived by subtracting from the appropriate experimental ionisation potential (see Appendix) the relativistic Dirac–Fock prediction. The latter is calculated as the difference between the total energy of the single-configuration Dirac–Fock $(N-1)$-electron wavefunction for the cation and the energy of the N-electron Dirac–Fock wavefunction containing a single valence s electron. The use of Dirac–Fock rather than Hartree–Fock ionisation potentials will yield more accurate values for the required non-relativistic correlation energy differences because this procedure eliminates relativistic effects inherent in the experimental results except for the very small relativistic correlation contributions to the ionisation potentials. It is shown in the Appendix that neither the Breit interaction, accurately computed, nor the Lamb shift, approximately calculated, contribute significantly to the ionisation potentials. However the experimental ionisation potentials of the first row elements need to be corrected for nuclear motion (see Appendix).

The correlation contributions to $\Delta\sigma(M)$ predicted from (8) using the cubic approximation are presented in table 2. In the Appendix it is shown not only that the cubic approximation to $(dI_{corrM}(Z)/dZ)_{Z=Z_M}$ is slightly preferable to the quadratic one, but also that the values of $\Delta\sigma_{corr}(M)$ predicted using the two approximations, see table 2, do not differ by more than 16%. Even the values for $\Delta\sigma_{corr}(M)$ predicted using the linear approximation to $(dI_{corrM}(Z)/dZ)_{Z=Z_M}$ do not differ from those given in table 2 by more than 20%. The reliability of table 2 can be further checked by comparing the results of accurate *ab initio* calculations with the predictions of (7) for the correlation contributions to the total shieldings of Li^+ and of Li. Thus the value for $\sigma_{corr}(Li^+)$ of 0.0172 ppm derived from (7) using the cubic approximation to $(d(E_{exLi^+}(Z) - E_{HFLi^+}(Z))/dZ)_{Z=3}$ agrees almost perfectly with the exact result of 0.0179 ppm calculated from Z-expansion perturbation theory carried through to tenth order as described in the Appendix. Although *ab initio* results of such high quality are not currently available for Li, the discrepancy between the prediction from (7) of $\sigma_{corr}(Li) = 0.0450$ ppm and the *ab initio* value of 0.0403 ppm (see appendix) is no greater than the probable error in the *ab initio* value as gauged from the difference 0.00092 au between the computed and exact kinetic energy.

Table 2. Alkali-atom–cation shielding difference predictions ($\Delta\sigma(M)$) with electron correlation (ppm).

M	$\Delta\sigma_{corr}(M)$†	$\Delta\sigma_{th}(M)$‡	$\Delta\sigma_{expt}(M)$§
Li	0.028	6.074	
Na	0.090	5.179	
K	0.145	4.078	29 ± 6
Rb	0.180	3.773	3.8 ± 2.6
Cs	0.141	3.310	-7.1 ± 2.0

† Derived via equation (8) using cubic fits to the correlation contributions ($I_{corrM}(Z)$, table A5) to the experimental ionisation potentials corrected for nuclear motion, Breit interaction and Lamb shift.
‡ Best theoretical value $\Delta\sigma_{th}(M) = \Delta\sigma_{HF}(M) + \Delta\sigma_{corr}(M)$.
§ See footnote to table 1.

The results of table 2 show that electron correlation slightly increases $\Delta\sigma(M)$. It can be concluded that electron correlation makes only a small contribution to the neutral–cation shielding difference $\Delta\sigma(M)$, and hence that this is not responsible for the discrepancies between the theoretical and experimental results for $\Delta\sigma(K)$ and $\Delta\sigma(Cs)$.

3. Dependence of nuclear shielding on ionisation state

In this section it is shown that shielding in a neutral atom is greater than that in its first positive ion.

Since the total energy of a neutral atom is lower than that of its first positive ion, it follows from the virial theorem that the total potential energy, composed of the electron–nuclear attraction plus the interelectron repulsion, of the atom is more negative than that of the first positive ion. It immediately follows that the total interelectron

repulsion of the neutral atom would have to be less than that of the first positive ion if the nuclear shielding in the neutral really was less than that of the positive ion, i.e. if $\Delta\sigma(M)$ were negative. This is extremely unlikely. Furthermore, since the virial theorem shows that the kinetic energy of M is greater than that of M^+, it would follow that if $\sigma(M)$ were less than $\sigma(M^+)$, then the valence s electron of an alkali metal is bound not by the attraction for the nucleus but by a reduction of the total interelectron repulsion.

The exact shielding difference, $\Delta\sigma_{ex}(M)$, can be related to the Z dependence of the first ionisation potential, $I_M(Z)$. Application of the Hellmann–Feynman theorem to the derivative with respect to Z of the exact energies $E_{exM}(Z)$ and $E_{exM^+}(Z)$ yields

$$\Delta\sigma_{ex}(M) = \sigma_{ex}(M) - \sigma_{ex}(M^+) = -\frac{1}{3c^2}\left[\left(\frac{dE_{exM}(Z)}{dZ}\right)_{Z=Z_M} - \left(\frac{dE_{exM^+}(Z)}{dZ}\right)_{Z=Z_M}\right]$$

i.e.

$$\Delta\sigma_{ex}(M) = \frac{1}{3c^2}\left(\frac{dI_M(Z)}{dZ}\right)_{Z=Z_M}. \tag{10}$$

This result immediately shows that $\Delta\sigma_{ex}(M)$ must be positive because all ground-state ionisation potentials belonging to an isoelectronic sequence increase with increasing Z (Moore 1971).

The reliability of (10) can be checked by deriving the total neutral-cation shielding differences $(\Delta\sigma(M))$ from the experimental ionisation potentials of the alkali metals, alkaline earths and the group IIIA and IVA elements. Although the use of experimental ionisation potentials does not eliminate the relativistic contributions, these are almost negligible as evidenced by the 0.0045 au relativistic contribution to the first ionisation potential of Cs calculated as the difference between the Dirac–Fock and Hartree–Fock ionisation potential predictions. The shielding differences $\Delta\sigma(M)$ predicted from (10) by using linear, quadratic and cubic fits to $I_M(Z)$ are presented in table 3. Even the predictions from the less reliable linear fits not only reproduce semi-quantitatively the results of table 2 but also show conclusively that $\Delta\sigma(M)$ is positive. The results derived from both the quadratic and cubic fits are significantly more trustworthy, almost exactly reproducing the most reliable predictions of $\Delta\sigma(M)$ given in table 2. It can therefore be concluded that $\Delta\sigma(M)$ is positive in sharp disagreement with the experimental result reported (Oluwole 1977) for Cs.

Table 3. Theoretical alkali-atom-cation shielding differences $(\Delta\sigma_{th}(M))$ compared with those derived solely from experiment (ppm).

M	$\Delta\sigma(M)$ from (10)[†]			$\Delta\sigma_{th}(M)$[‡]
	Linear	Quadratic	Cubic	
Li	8.362	6.111	6.099	6.074
Na	6.455	5.308	5.257	5.179
K	4.912	4.197	4.148	4.078
Rb	4.470	3.921	3.879	3.773
Cs	3.986	3.536	3.462	3.310

† Derived from equation (10) using experimental ionisation potentials $(I_M(Z))$ reported in table A5 of the Appendix. Fit types, linear, quadratic or cubic, defined in text.
‡ Best theoretical value $= \Delta\sigma_{HF}(M) + \Delta\sigma_{corr}(M)$.

4. Conclusion

The differences $\Delta\sigma(M)$ between the nuclear shieldings in alkali atoms and in their first positive ions have been calculated from non-relativistic Hartree–Fock theory. The corrections to $\Delta\sigma(M)$ arising from electron correlation have been derived through the Hellmann–Feynman theorem by combining Dirac–Fock and experimental ionisation potentials and are shown to be small. A further argument based on the Hellmann–Feynman theorem shows that $\Delta\sigma(M)$ is positive. This is used in conjunction with experimental data to derive values in close agreement with the essentially *ab initio* results for $\Delta\sigma(M)$. Two highly approximate methods for calculating $\Delta\sigma(M)$ previously reported (Davis *et al* 1974, Oluwole 1977, Obiajunwa *et al* 1983) have been shown to be quite inadequate.

The theoretical and experimental results for the shielding difference $\Delta\sigma(Rb)$ agree but qualitative and quantitative discrepancies between theory and experiment for both $\Delta\sigma(K)$ and $\Delta\sigma(Cs)$ cannot be explained by errors in the theory. The present theoretical calculations of nuclear shieldings have been shown to be reliable. Thus it is how highly desirable that the experimental measurements and their analysis should be re-examined and it would be particularly interesting if $\Delta\sigma(K)$, $\Delta\sigma(Rb)$ and $\Delta\sigma(Cs)$ were to be remeasured in a single series of experiments.

Appendix

A.1. Comparison of calculations of correlation contribution to shieldings

For the two-electron isoelectronic sequence the non-relativistic Hartree–Fock energies $(E_{HF2}(Z))$ computed by running the Oxford Dirac–Fock programme with a large value of the velocity of light, the exact non-relativistic energies $(E_{ex2}(Z))$ (Frankowski and Pekeris 1966) and the correlation energies $(E_{corr2}(Z) = E_{ex2}(Z) - E_{HF2}(Z))$ are presented in table A1. These correlation energies differ slightly from those used previously (Mazziotti 1970) in a similar calculation of the correlation contribution $(\sigma_{corr2}(Z))$ to the nuclear shielding because the Hartree–Fock energies of table A1 are slightly lower than those used by Mazziotti which were computed (Clementi 1965) by the basis set expansion technique. This table also presents the Hartree–Fock prediction $(\langle r^{-1}\rangle_{HF})$ for $\langle r^{-1}\rangle$ and the exact results $(\langle r^{-1}\rangle_{ex})$ computed from the $\langle r^{-1}\rangle$ coefficients calculated from sixth-order Z-expansion perturbation theory (Scherr and Knight 1964).

Table A1. Correlation energies and $\langle r^{-1}\rangle$ for two-electron systems (au)†.

	$-E_{ex2}(Z)$	$-E_{HF2}(Z)$	$-E_{corr2}(Z)$	$\langle r^{-1}\rangle_{ex}$	$\langle r^{-1}\rangle_{HF}$
H⁻	0.527 750	0.487 930	0.039 820		1.371 344
He	2.903 724	2.861 680	0.042 044	3.376 633	3.374 565
Li⁺	7.279 913	7.236 416	0.043 497	5.375 848	5.374 839
Be²⁺	13.655 566	13.611 299	0.044 267	7.375 501	7.374 917
B³⁺	22.030 972	21.986 235	0.044 737	9.375 328	9.374 949
C⁴⁺	32.406 247	32.361 193	0.045 054	11.375 231	11.374 966
N⁵⁺	44.781 445	44.736 164	0.045 281	13.375 171	13.374 976
O⁶⁺	59.156 595	59.111 143	0.045 452	15.375 132	15.374 982

† For definitions see text.

For Li$^+$ the calculation needed to be extended to higher order, the coefficients up to tenth order being derived through the Hellmann–Feynman theorem from the energy series calculated by Midtdal (1965).

The slope $(\mathrm{d}E_{\mathrm{corr}N}(Z')/\mathrm{d}Z')_{Z'=Z}$ needed to derive the correlation contribution $\sigma_{\mathrm{corr}N}(Z)$ to the shielding of the N-electron system having nuclear charge Z through

$$\sigma_{\mathrm{corr}N}(Z) = -\frac{1}{3c^2}\left(\frac{\mathrm{d}E_{\mathrm{corr}N}(Z')}{\mathrm{d}Z'}\right)_{Z'=Z} \tag{A.1}$$

must be calculated by differentiation of some analytic function reproducing the correlation energies considered. A linear approximation to $\sigma_{\mathrm{corr}N}(Z)$ is derived from the pair of correlation energies $E_{\mathrm{corr}N}(Z)$ and $E_{\mathrm{corr}N}(Z+1)$, a quadratic one by using also $E_{\mathrm{corr}N}(Z+2)$ whilst a cubic approximation is calculated from the four correlation energies $E_{\mathrm{corr}N}(Z)$ to $E_{\mathrm{corr}N}(Z+3)$. A variant of each of these predictions is generated by replacing $E_{\mathrm{corr}N}(Z+m)$ for the largest m considered by $E_{\mathrm{corr}N}(Z-1)$. In table A2 the predictions of these six different methods for deriving $\sigma_{\mathrm{corr}2}(Z)$ are compared with the exact results calculated by differencing the exact and Hartree–Fock $\langle r^{-1}\rangle$ values presented in table A1. The results show that a cubic fit to the correlation energies of the ion of interest and of the three ions of higher nuclear charge yields the most reliable values for $\sigma_{\mathrm{corr}2}(Z)$. The results also show both that $\sigma_{\mathrm{corr}2}(Z)$ is predicted slightly less accurately from quadratic fits to $E_{\mathrm{corr}2}(Z-1)$, $E_{\mathrm{corr}2}(Z)$ and $E_{\mathrm{corr}2}(Z+1)$ (Mazziotti 1970) and that linear fits introduce appreciable errors.

Table A2. Comparison between exact correlation contributions to nuclear shielding in two-electron systems with values derived from correlation energies (ppm).

	$\sigma_{\mathrm{corr}2}(Z)$ from correlation energies, equation (A.1)						
	Linear, $Z, Z+1$†	Linear, $Z-1, Z$†	Quadratic, $Z, Z+1,$ $Z+2$†	Quadratic, $Z-1, Z,$ $Z+1$†	Cubic, $Z, Z+1,$ $Z+2, Z+3$†	Cubic, $Z-1, Z,$ $Z+1, Z+2$†	Exact $\sigma_{\mathrm{corr}2}(Z)$
H$^-$	0.039 5		0.046 3		0.046 8		
He	0.025 8	0.039 5	0.031 9	0.032 6	0.034 1	0.032 4	0.036 7
Li$^+$	0.013 7	0.025 8	0.016 3	0.019 7	0.017 2	0.018 6	0.017 9
Be^{2+}	0.008 34	0.013 7	0.009 70	0.011 0	0.010 1	0.010 6	0.010 4
B^{3+}	0.005 63	0.008 34	0.006 43	0.006 98	0.006 63	0.006 80	0.006 73
C^{4+}	0.004 03	0.005 63	0.004 53	0.004 83		0.004 73	0.004 70
N^{5+}	0.003 04	0.004 03		0.003 53			0.003 46
O^{6+}		0.003 04					0.002 66

† Fits $\mathrm{d}E_{\mathrm{corr}2}(Z)/\mathrm{d}Z$ calculated as: $E_{\mathrm{corr}2}(Z+1)-E_{\mathrm{corr}2}(Z)$, linear, $Z, Z+1$; $E_{\mathrm{corr}2}(Z)-E_{\mathrm{corr}2}(Z-1)$, linear, $Z, Z-1$; $[4E_{\mathrm{corr}2}(Z+1)-3E_{\mathrm{corr}2}(Z)-E_{\mathrm{corr}2}(Z+2)]/2$, quadratic, $Z, Z+1, Z+2$; $[E_{\mathrm{corr}2}(Z+1)-E_{\mathrm{corr}2}(Z-1)]/2$, quadratic, $Z-1, Z, Z-1$; $[2E_{\mathrm{corr}2}(Z+3)-9E_{\mathrm{corr}2}(Z+2)+18E_{\mathrm{corr}2}(Z+1)-11E_{\mathrm{corr}2}(Z)]/6$, cubic, $Z, Z+1, Z+2, Z+3$; $[-2E_{\mathrm{corr}2}(Z-1)-3E_{\mathrm{corr}2}(Z)+6E_{\mathrm{corr}2}(Z+1)-E_{\mathrm{corr}2}(Z+2)]/6$, cubic, $Z-1, Z, Z+1, Z+2$.

Since *ab initio* results for $\sigma_{\mathrm{corr}N}(Z)$ of comparable quality are unavailable for any other systems, the two-electron results of table A2 necessarily constitute the backbone of the evidence on which the preference for cubic fits to $E_{\mathrm{corr}N}(Z)$, $E_{\mathrm{corr}N}(Z+1)$, $E_{\mathrm{corr}N}(Z+2)$ and $E_{\mathrm{corr}N}(Z+3)$ is based. However, this conclusion is not inconsistent with the comparison between the *ab initio* and experimentally derived $\sigma_{\mathrm{corr}4}(Z)$ values

for the four-electron systems presented in table A4. The total correlation energies $(E_{corr4}(Z)$, table A3) were derived by adding the correlation energies $(E_{corr2}(Z))$ of the two-electron systems (table A1) to the sum of the correlation contributions to the two processes $1s^2 2s^2 \rightarrow 1s^2 2s$ and $1s^2 2s \rightarrow 1s^2$. The methods used to extract the latter two contributions from experiment are described in the next section. It should be pointed out that the discrepancies between the *ab initio* and experimentally derived values of $\sigma_{corr4}(Z)$ for the four-electron systems are just as likely to arise from inadequacies in the correlated wavefunctions (Sabelli and Hinze 1969) as from deficiencies in the fitting procedures.

Table A3. Total correlation energies $(E_{corr4}(Z))$ of four-electron systems (au).

| | Dirac–Fock IP (I_{DF})† | −Corrections to ionisation potential | | Experimental IP‖ | |
		Breit $(-I_{Br})$‡	$-I_{LS}$§	(I_{expt})	$-E_{corr4}(Z)$¶
Li⁻	−0.004 495	0.000 001	0.000 000	0.022 785	0.072 617
Be	0.295 677	0.000 012	0.000 004	0.342 601	0.094 333
B⁺	0.861 835	0.000 048	0.000 021	0.924 414	0.111 344
C²⁺	1.683 190	0.000 114	0.000 060	1.759 473	0.126 047
N³⁺	2.757 231	0.000 221	0.000 126	2.847 031	0.140 408
O⁴⁺	4.083 195	0.000 380	0.000 234	4.185 914	0.154 127

† Ionisation potential for process $1s^2 2s^2 \rightarrow 1s^2 2s$.
‡ I_{Br} = Breit energy of $1s^2 2s$ − Breit energy of $1s^2 2s^2$; calculated exactly.
§ I_{LS} = Lamb shift contribution to ionisation potential calculated as $(\varepsilon_{LS}$ in $1s^2 2s$ state$) - 2(\varepsilon_{LS}$ in $1s^2 2s^2$ state) with the Lamb shift energy ε_{LS} of one 2s electron calculated from (A.2).
‖ From Moore (1949) except Li⁻ from Patterson *et al* (1974) with last two figures not significant.
¶ Total correlation energy $E_{corr4}(Z) = E_{corr2}(Z) - I_{corrLi}(Z) - I_{expt} + I_{DF} + I_{Br} + I_{LS} - I_{expt}/M_n$, $E_{corr2}(Z)$ from table A1, $I_{corrLi}(Z)$ from table A5 for Li to C³⁺ and computed as $E_{corr2}(Z) - E_{corr3}(Z)$ (tables A1 and A7) for N⁴⁺ and O⁵⁺. I_{expt}/M_n is the nuclear motion correction with M_n the nuclear mass.

Table A4. Comparison between *ab initio* correlation contributions to nuclear shielding in four-electron systems with values derived from correlation energies (ppm).

| | $\sigma_{corr4}(Z)$ from correlation energies; equation (A.1) | | | *Ab initio* $\sigma_{corr4}(Z)$ | | |
	Linear $Z, Z+1$†	Quadratic $Z, Z+1, Z+2$†	Cubic $Z, Z+1, Z+2, Z+3$†	Unscaled‡	Scaled§	$\langle r^{-1} \rangle_{HF}$
Li⁻	0.385	0.427	0.441	0.440	0.440	5.870 00
Be	0.302	0.322	0.334	0.295	0.296	8.408 80
B⁺	0.261	0.264	0.262	0.237	0.241	10.918 65
C²⁺	0.255	0.261		0.236	0.233	13.422 69

† Fits defined as in first footnote to table A2 with E_{corr2} replaced by E_{corr4}.
‡ Calculated by dividing by $3c^2$ the difference between correlated $\langle r^{-1} \rangle$ (Sabelli and Hinze 1969) and $\langle r^{-1} \rangle_{HF}$ presented here.
§ Derived by multiplying correlated $\langle r^{-1} \rangle$ values by $(-E + \langle T \rangle)/(2\langle T \rangle)$ where E and $\langle T \rangle$ are the total and kinetic energies of the correlated wavefunction (Sabelli and Hinze 1969). This factor yields the $\langle r^{-1} \rangle$ predicted by this wavefunction after scaling to satisfy the virial theorem exactly.

The results (table 3 of the main paper) for the total shielding differences $\Delta\sigma(M)$ derived through (10) from experimental ionisation potentials also suggest that cubic fits to the system of interest and those of higher nuclear charge are most trustworthy. Thus both the quadratic and cubic, unlike the linear fits, almost exactly reproduce the large Hartree-Fock plus small correlation shielding differences $\Delta\sigma(M)$. Finally it should be pointed out that cubic fits involving the species of nuclear charge $Z_M - 1$ are possible neither for the neutral alkalis nor for the ionisation process core s → core because the referenced inert-gas anions do not exist.

A.2. Data used to derive $\Delta\sigma_{corr}(M)$ results for the alkali metals

The Dirac-Fock and experimental ionisation potentials ($I_M(Z)$) for the removal of a single-valence s electron from the neutral alkalis, from the first positive ions of the alkaline earths, from the second positive ions of the Group IIIA elements and from the third positive ions of the Group IVA elements are reported in table A5. Since the

Table A5. Correlation corrections ($I_{corrM}(Z)$) to ionisation potentials $I_M(Z)$ for removal of a valence s electron (au).

	Dirac-Fock $I_M(Z)(I_{DF})$†	−Correction to $I_M(Z)$		Experimental $I_M(Z)\|$	
		Breit $(-I_{Br})$‡	ε_{LS}§	(I_{expt})	$I_{corrM}(Z)$¶
Li	0.196 328	0.000 004	0.000 002	0.198 142	0.001 835
Na	0.182 182	0.000 010	0.000 017	0.188 858	0.006 708
K	0.147 752	0.000 010	0.000 032	0.159 516	0.011 808
Rb	0.139 655	0.000 013	0.000 089	0.153 508	0.013 956
Cs	0.127 788	0.000 013	0.000 141	0.143 099	0.015 465
Be$^+$	0.666 214	0.000 024	0.000 012	0.669 242	0.003 105
Mg$^+$	0.541 826	0.000 042	0.000 056	0.552 535	0.010 820
Ca$^+$	0.417 268	0.000 039	0.000 092	0.436 260	0.019 129
Sr$^+$	0.383 749	0.000 055	0.000 228	0.405 350	0.021 887
Ba$^+$	0.344 201	0.000 061	0.000 345	0.367 636	0.023 842
B^{2+}	1.390 182	0.000 064	0.000 037	1.393 925	0.003 913
Al^{2+}	1.032 206	0.000 095	0.000 119	1.045 469	0.013 498
Sc^{2+}	0.769 114	0.000 086	0.000 172	0.793 546	0.024 700
Y^{2+}	0.693 053	0.000 121	0.000 395	0.719 094	0.026 561
La^{2+}	0.613 470	0.000 135	0.000 577	0.642 825	0.030 070
C^{3+}	2.365 976	0.000 134	0.000 086	2.370 104	0.004 456
Si^{3+}	1.643 948	0.000 174	0.000 208	1.658 951	0.015 417
Ti^{3+}	1.195 086	0.000 151	0.000 275	1.223 099	0.028 453
Zr^{3+}	1.058 822	0.000 208	0.000 591	1.087 665	0.029 649
Ce^{3+}	0.927 598	0.000 232	0.000 837	0.956 229	0.029 702

† Ionisation potential for process core ns → core in system with nuclear charge Z and core isoelectronic with that of alkali metal M.
‡ I_{Br} = Total Breit energy of cation − total Breit energy of neutral.
§ ε_{LS} = Lamb shift energy of valence s electron calculated from (A.2).
$\|$ From Moore (1949, 1952, 1958), except Zr from Moore (1971) and La and Ce from Martin *et al* (1978). All figures not significant in a few cases.
¶ $I_{corrM}(Z) = I_{expt} - I_{DF} - I_{Br} + \varepsilon_{LS} + I_{expt}/M_n$. I_{expt}/M_n is the nuclear motion correction with M_n the nuclear mass.

ground configurations of Sc^{2+}, Y^{2+}, La^{2+}, Ti^{3+}, Zr^{3+} and Ce^{3+} contain a single-valence d or f electron, the experimental ionisation potentials were derived by subtracting the experimental d→s or f→s excitation energies (Moore 1949, 1952, 1958, Martin *et al* 1978) from the ionisation potentials reported by Moore (1949, 1952, 1958, 1971) and Martin *et al* (1978). The contributions (table A5) to the ionisation potentials which arise from the Breit interaction (Breit 1929, 1930) were computed exactly using the Oxford Dirac-Fock program (Grant *et al* 1976, 1980, Grant and Pyper 1976) as the difference between the total Breit energies of the neutral and cation Dirac-Fock wavefunctions.

The very small quantum electrodynamic contributions to the ionisation potentials were estimated assuming that these are dominated by the valence-electron Lamb shift thus neglecting the difference between the quantum electrodynamic energies of the neutral and cation cores. The leading term in the Lamb shift energy (ε_{LS}) of the valence electron is given by (Kabir and Salpeter 1957)

$$\varepsilon_{LS} = \langle V_Z(M)|\nabla^2 \hat{V}| V_Z(M)\rangle(\ln c^2 - \ln \bar{E} - \ln 2 + \tfrac{19}{30})(3\pi c^3)^{-1}. \qquad (A.2)$$

Here $\hat{V}$ is the Hartree-Fock potential experienced by the valence electron, $\ln \bar{E}$ is the Bethe logarithm (Bethe *et al* 1950) and $V_Z(M)$ is the spatial valence s orbital of the system of nuclear charge Z and isoelectronic with M so that $V_M(Z) = V(M)$. The quantity $\langle V_Z(M)|\nabla^2 \hat{V}| V_Z(M)\rangle$, which is a sum of a nuclear term $\langle V_Z(M)|\nabla^2 \hat{V}_{nuc}| V_Z(M)\rangle$ with $\hat{V}_{nuc}$ the nuclear potential plus a purely electronic part, also arises (Pyper 1980, Pyper and Marketos 1981) in the Darwin relativistic correction to the non-relativistic valence electron energy. Since the contribution arising from the electronic part of $\nabla^2 \hat{V}$ is only 1% of $\langle V_Z(M)|\nabla^2 \hat{V}_{nuc}| V_Z(M)\rangle$ except for the second and first row systems where the electronic part is 2% and 5% (Pyper and Marketos 1981), the electronic part of $\nabla^2 \hat{V}$ will be neglected. The Bethe logarithm is related to the moments of the oscillator strength distributions (Fano and Cooper 1968) through

$$\ln \bar{E} = (d \ln S(x)/dx)_{x=2} - \ln 2. \qquad (A.3)$$

These derivatives will be estimated from the linear approximation generated by the values of $S(1)$ and $S(2)$ which were computed through (Fano and Cooper 1968)

$$\begin{aligned} S(1) &= 8\langle V_Z(M)| -\tfrac{1}{2}\nabla^2| V_Z(M)\rangle/3 \\ S(2) &= 16\pi Z\langle V_Z(M)|\delta(0)| V_Z(M)\rangle/3 \end{aligned} \qquad (A.4)$$

from the Hartree-Fock wavefunctions.

The reduced mass correction is the leading contribution to the ionisation potential arising from nuclear motion. Since this correction to the non-relativistic total energy of an atom is given by dividing this energy by the nuclear mass (Hughes and Eckart 1930), the correction to the non-relativistic ionisation potential is just this potential divided by the nuclear mass. Since the relativistic and nuclear motion corrections constitute only a small fraction of the total ionisation potential, the mass corrections were calculated from the experimental ionisation potentials.

The correlation contributions ($I_{corrM}(Z)$) to the ionisation potentials calculated as the difference between the experimental results and the sum of the Dirac-Fock prediction plus nuclear motion, Breit and quantum electrodynamic corrections are presented in table A5. The correlation contribution ($\Delta\sigma_{corr}(M)$) to the alkali-atom–cation nuclear shielding differences predicted through (8) from linear, quadratic and cubic fits to the Z dependence of $I_{corrM}(Z)$ are presented in table A6. The predictions of $\Delta\sigma_{corr}(M)$

Table A6. Comparison of different methods for calculating of $\Delta\sigma_{corr}(M)$ for the alkali metals (ppm) from equation (8).

	$\Delta\sigma_{corr}(M)$ from fully corrected ionisation potentials‡			$\Delta\sigma_{corr}(M)$ from uncorrected IP§
	Linear, $Z, Z+1$†	Quadratic, $Z, Z+1,$ $Z+2$†	Cubic, $Z, Z+1,$ $Z+2, Z+3$†	cubic, $Z, Z+1,$ $Z+2, Z+3$
Li	0.0225	0.0266	0.0278	0.0270
Na	0.0730	0.0857	0.0897	0.0886
K	0.130	0.146	0.145	0.144
Rb	0.141	0.170	0.180	0.177
Cs	0.149	0.168	0.141	0.137

† Fits defined as in first footnote to table A2 with E_{corr2} replaced by I_{corrM}.
‡ Derived from $I_{corrM}(Z)$ values of table A5.
§ Derived from $I_{corrM}(Z)$ values $(=I_{expt} - I_{DF})$ uncorrected for nuclear motion, Breit interaction or Lamb shift. I_{expt} and I_{DF} taken from table A5.

derived from $I_{corrM}(Z)$ values which are not corrected for nuclear motion, Breit interaction or quantum electrodynamic effects do not differ significantly (table A6) from those calculated using the corrected results for $I_{corrM}(Z)$.

A.3. The correlation contributions to the shielding in three-electron atoms

The correlation contribution $(I_{corrLi}(Z))$ to the ionisation potential $(I_{Li}(Z))$ for the removal of the 2s electron in each member of the three-electron isoelectronic sequence was calculated as described previously. The total correlation energies of these systems $(E_{corr3}(Z)$, table A7) were calculated by adding to the experimentally derived values of $I_{corrLi}(Z)$, the correlation energies $(E_{corr2}(Z)$, table A1) of the two electron systems.

The correlation contributions $(\sigma_{corr3}(Z))$ to the total nuclear shieldings derived from the *ab initio* calculations of Cooper and Martin (1963) are compared in table A8 with the predictions calculated from (A.1) using cubic fits to the Z dependence of $E_{corr3}(Z)$. For Be^+ and B^{2+} these results differ slightly from those derived previously (Mehrotra and Saxena 1975) both because the present correlation energies are slightly different and because cubic fits to the Z dependence, which have been shown to be

Table A7. Total correlation energies $(E_{corr3}(Z))$ of three-electron systems†.

	Dirac–Fock $I_{Li}(Z)(I_{DF})$	− Correction to $I_{Li}(Z)$		Experimental $I_{Li}(Z)$	
		Breit $(-I_{Br})$	ε_{LS}	(I_{expt})	$-E_{corr3}(Z)$‡
N^{4+}	3.593 069	0.000 252	0.000 170	3.597 376	0.050 150
O^{5+}	5.071 424	0.000 396	0.000 300	5.075 755	0.050 652

† See first three footnotes to table A5.
‡ Total correlation energy $E_{corr3}(Z) = E_{corr2}(Z) - I_{expt} + I_{DF} + I_{Br} - \varepsilon_{LS} - I_{expt}/M_n$, I_{expt}/M_n is the nuclear motion correction. For Li to C^{3+} the total correlation energies needed are given by $E_{corr2}(Z) - I_{corrLi}(Z)$, with $E_{corr2}(Z)$ in table A1 and $I_{corrLi}(Z)$ in table A5.

Table A8. Comparison between *ab initio* correlation contributions to nuclear shielding in three-electron systems with values derived from correlation energies (ppm)†.

| | $\sigma_{\text{corr3}}(Z)$ from correlation energies, equation (A1) | | | *Ab initio* $\sigma_{\text{corr3}}(Z)$ | | |
	Linear $Z, Z+1$	Quadratic, $Z, Z+1,$ $Z+2$	Cubic, $Z, Z+1,$ $Z+2, Z+3$	Unscaled‡	Scaled	$\langle r^{-1}\rangle_{\text{HF}}$
Li	0.0362	0.0430	0.0450	0.0362	0.0403	5.715 460
Be⁺	0.0227	0.0267	0.0286	0.0082	0.0171	7.972 338
B²⁺	0.0153	0.0172	0.0177	0.0120	0.0138	10.224 525

† See first three footnotes to table A4 with E_{corr4} replaced by E_{corr3} in the first.
‡ From Cooper and Martin (1963).

most trustworthy, have been used rather than quadratic ones. Since the *ab initio* wavefunctions do not exactly satisfy the virial theorem, scaling of these functions yields the improved *ab initio* predictions also reported. The discrepancies between the experimentally derived and the *ab initio* values for $\sigma_{\text{corr3}}(Z)$ probably arise from inadequacies in the *ab initio* wavefunctions. Indeed for Li the discrepancy (0.00026 au in $\langle r^{-1}\rangle$) is no greater than the probable error in the *ab initio* value as estimated from the difference (0.00092 au) between the scaled *ab initio* kinetic energy and the exact kinetic energy of 7.478060 (= the Hartree-Fock value plus the correlation energy reported in table A8).

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