

Long-range effects of interatomic interactions on NMR shielding constants

Andrzej Barszczewicz ^a, Michał Jaszuński ^a, Trygve Helgaker ^b, Kenneth Ruud ^b

^a *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01 224 Warsaw, Poland*

^b *Department of Chemistry, University of Oslo, P.O.B. 1033, Blindern, N-0315 Oslo, Norway*

Received 25 September 1995; in final form 29 December 1995

Abstract

The effect of the weak long-range interaction on the shielding constant is considered for a pair of interacting atoms. The asymptotic long-range effects are proportional to R^{-n} (where R is the interatomic distance). For the anisotropy of the shielding tensor $n = 3$, for the trace $n = 6$ for two neutral atoms and $n = 4$ for the atom shielding in an atom–ion pair. Calculations on the He–He system, using a full-CI expansion and on the Ar–Na⁺ interaction, using an SCF wavefunction, confirm the expected long-range dependence of the change in the shielding constant.

1. Introduction

The dependence of atomic polarizabilities on weak long range interactions has been studied in detail [1,2]. For a diatomic system, the asymptotic dependence both of the anisotropy and of the average of the polarizability tensor can be expressed as a series in R^{-n} where R is the interatomic distance. The role of correlation effects is understood, and the SCF and correlation contributions to the R^{-n} expansion coefficients can be determined [1–4].

More recently, similar long range effects have been studied for NMR shielding constants [5–9]. The effects of the intermolecular forces have been analysed primarily within an approach commonly used for polarizabilities, where the interaction is described by considering the electric field generated by the other atom.

We use here a different approach. We assume that for the supermolecule consisting of a pair of weakly interacting subsystems the shielding can be calculated as for any other molecule, i.e. as the second derivative of the energy with respect to the external magnetic field and the field due to the nuclear magnetic moment. Consequently, the effect of the van der Waals interaction on the NMR shielding corresponds to the second derivative of the interaction energy. All calculations have been performed on the supermolecule, but in the interpretation of the results we apply concepts taken from the perturbation theory of weak interactions. Such an approach has been successful in studies of weak intermolecular forces (see e.g. the recent review [10] and references therein).

We concentrate here on the long-range interactions. Although the effects may be so small that they

can hardly be observed (a fraction of a ppm), several advantages are obtained in an approach based on ab initio calculations at large R values. We do not need to consider explicitly the overlap and exchange effects, so we can use the asymptotic R^{-n} expansion. We may relate the expansion coefficients to other atomic properties and in many cases also accurately compute these coefficients. This enables a useful comparison of the supermolecule calculations with a long-range expansion which treats the interaction as a perturbation. Moreover, we can determine from such a comparison the region of interatomic distances for which the long range expansion is valid.

2. Theory

There are two significant differences between the effect of intermolecular forces on the polarizability and on the shielding. The long-range multipole expansion of the interaction operator,

$$V_{AB} = -ez_A q_B / R^2 + e(x_A^2 + y_A^2 - 2z_A^2)q_B / 2R^3 + e(x_A x_B + y_A y_B + 2z_A z_B) / R^3 + \dots, \quad (1)$$

includes by definition only electric multipole operators. To simplify the notation we have assumed that q_A , the charge of atom A, is zero, as we shall not study the interactions of two charged systems. In a perturbation expansion of incremental polarizabilities, we obtain contributions of the type $\langle 0 | z | n \rangle \times \langle n | z / R^3 | 0 \rangle$, where $|0\rangle$ and $|n\rangle$ are the states of atom A, the z operator represents the external electric field perturbation and the z/R^3 operator comes from V_{AB} . For the shielding of an atom in a diatomic molecule there is by symmetry no state $|n\rangle$ coupling the external perturbation (angular momentum operator) with V_{AB} . Thus, there is a difference between the effect of intermolecular forces on the electric dipole polarizability, where even at the SCF level one observes an R^{-6} contribution, and the effect on the shielding, where the only R^{-6} term comes from dispersion.

On the other hand, the appropriate perturbation operators now contain r_{iX}^{-3} , where $X = A$ or B for the shielding of atom A or B, respectively. This

means that when computing σ_A we can separate the terms proportional to R^{-3} due to orbitals of atom B. We follow here the interpretation of Hansen and Bouman [11], recalling that once the calculations are sufficiently accurate, the same R^{-n} -asymptotic dependence is obtained whether localised orbitals are used or not. In particular, this interpretation shows that there is a difference in the asymptotic dependence of the interatomic interaction effects on the isotropic shielding and on the anisotropy (see below).

We use for the effect of the long-range interaction on the shielding the symbol δ_X , and for each nucleus the reference value is the shielding of the isolated atom (the ion for Na^+). For a given interatomic distance R

$$\delta_X(R) = \sigma_X(\text{in } X\text{-}Y \text{ at } R) - \sigma_X(\text{isolated } X). \quad (2)$$

For the anisotropy of the shielding tensor we shall use the standard symbol $\Delta\sigma$. Since for an isolated atom $\Delta\sigma = 0$, the anisotropy is entirely due to the interatomic interaction. In the interaction of molecules (or an atom with a molecule), the effect of long-range interaction is proportional to the anisotropy of the magnetic susceptibility of the distant group [12]. A similar relation, which we shall use here, has been considered by Hansen and Bouman [11]. They discussed the effect on the shielding of a distant group (part of a molecule) and found it to be proportional to R^{-3} and dependent on the tensor

$$\mathbf{T} = \mathbf{1} - 3\mathbf{R} \cdot \mathbf{R} / R^2. \quad (3)$$

This indicates that in case of atom–atom interaction the terms proportional to R^{-3} cancel for the average shielding tensor, but not for the change of the anisotropy of the shielding.

In the calculations, we concentrate on two examples. The first is the He–He interaction. For this system more accurate calculations are possible than for the interactions of other rare gas atoms. The second example is the interaction of the Ar atom with a Na^+ ion and we consider the shielding of both Ar and Na^+ . To interpret the results, for both systems we consider the interaction energy which depends implicitly on the external magnetic field and the nuclear magnetic moments.

In the He–He interaction, the dominant term is the dispersion energy, which cannot be recovered in SCF calculations and we can only obtain the correct asymptotic form when correlation effects are incorporated. The proper expansion for the energy starts from $-C_6/R^6$, where C_6 can be expressed in terms of the atomic polarizability $\alpha(-i\omega; i\omega)$ as

$$C_6 = 3/\pi \int \alpha(-i\omega; i\omega) \alpha(-i\omega; i\omega) d\omega. \quad (4)$$

Therefore R^{-6} dependence is also expected for $\delta(R)$, the interaction effect on the shielding. To obtain the expansion coefficient for $\delta(R)$ we can differentiate Eq. (4) with respect to the external magnetic field and the nuclear magnetic moment. The corresponding derivatives of $\alpha(-i\omega; i\omega)$ can be reinterpreted as second derivatives of components of the shielding tensor σ with respect to an electric field. For an atom in a static electric field, analogous derivatives are called shielding polarizabilities and a linear combination of the tensor components is usually defined [7]

$$B = B(0; 0, 0, 0) = -\frac{1}{6} \left(\partial^2 \sigma_{\parallel} / \partial^2 F + 2 \partial^2 \sigma_{\perp} / \partial^2 F \right), \quad (5)$$

where σ_{\parallel} and σ_{\perp} denote the shielding tensor components parallel and perpendicular to the electric field F . Applying a similar notation we describe the R^{-6} expansion coefficient for $\delta(R)$ as proportional to $B(-i\omega; i\omega, 0, 0)$.

Similar expressions have been derived for the correlation contribution to interaction effects on polarizabilities [2]. Following the scheme used for polarizabilities, we can approximate the R^{-6} coefficient by

$$\begin{aligned} & -BC_6/\alpha \\ & \approx - \int B(-i\omega; i\omega, 0, 0) \alpha(-i\omega; i\omega) d\omega, \end{aligned} \quad (6)$$

which is the same coefficient as the one derived in another approach by Jameson and de Dios [6].

In the Ar–Na⁺ system there is an induction energy contribution of the form $-\alpha_{\text{Ar}} q_{\text{Na}}^2 / 2R^4$ which can be described in the SCF approach (q is the charge of an atom). The corresponding changes in the Ar shielding are obtained from the derivative, proportional to $-\partial^2 \alpha_{\text{Ar}} / \partial B_0 \partial \mu_{\text{Ar}} \cdot q_{\text{Na}}^2 / R^4$ where B_0

is the external magnetic field and μ the nuclear magnetic moment. Hence, we expect for δ_{Ar} an R^{-4} asymptotic dependence; the derivative is equal to $-B_{\text{Ar}} q_{\text{Na}}^2 / R^4$ and the same expansion coefficient has been obtained by Jameson and de Dios [6]. For the shielding of Na⁺, there are no R^{-4} contributions, and no R^{-6} terms which can be reproduced within the SCF approximation (an R^{-6} contribution due to dispersion interaction is not recovered in SCF).

3. Results and discussion

For the He–He system the first requirement is that the correlation effects have to be well described. We have used a variety of CASSCF calculations with rather large basis sets, but we found that the van der Waals energy minimum was much better described by a full-CI wavefunction with a smaller basis set. This is the approximation we have finally chosen and all He shielding constants discussed below thus refer to this full-CI calculation.

As mentioned above, the main effects of the interaction on the Ar atom shielding in Ar–Na⁺ can be described at the SCF level, and this is the approximation we used. Therefore, all the results reported for isolated atoms and the related asymptotic expansion parameters are given at the SCF level for this system.

High numerical accuracy of the calculations was required, and we use lower thresholds for neglecting the integrals, the convergence of the wavefunction and the convergence of the response equations than in standard shielding tensor calculations. For example, all the integrals are exact to 10^{-12} . Most importantly, there are significant basis set superposition errors (BSSE). We denote as δ_X^{BSSE} the difference between σ_X (in X–0 at R), that is the value of σ_X computed in a supermolecule basis set where the ghost basis is placed at a distance R from the atom, and the shielding of the isolated atom. Thus, assuming an implicit R dependence

$$\delta_X^{\text{BSSE}} = \sigma_X(\text{in X–0 at } R) - \sigma_X(\text{isolated X}). \quad (7)$$

In practice, the role of the ‘ghost’ basis was often more significant than the interaction effect itself, so the change of the shielding was dominated by BSSE, which is an artefact of the calculation. Even with large basis sets (e.g. in test calculations using 168 CGTOs for Ar–Na⁺) we have observed for many interatomic distances that δ^{BSSE} constituted over 90% of the $\delta(R)$ obtained from the original definition (2), with the isolated atom value taken as the reference. In the He–He and Ar–Na⁺ calculations we discuss below, the BSSE contribution is for most internuclear distances (with the exception of the region where $\delta(R)$ changes sign for Na⁺) much smaller, but nevertheless significant. Therefore, we systematically apply the standard counterpoise (CP) correction for the BSSE and redefine $\delta(R)$ as

$$\delta_X(R) = \sigma_X(\text{in X–Y at } R) - \sigma_X(\text{in X–0 at } R) \quad (8)$$

Only $\delta(R)$ and $\Delta\sigma$ values corrected in this way are analysed in detail.

Although by applying the CP correction for BSSE we improve the results significantly, it was not possible to establish the $\delta(R)$ values with sufficient accuracy at all distances. We therefore list the results for δ^{BSSE} and also for $\Delta\sigma^{\text{BSSE}}$, which is defined similarly to δ^{BSSE}

$$\Delta\sigma^{\text{BSSE}} = \Delta\sigma(\text{in X–O at } R) \quad (9)$$

(the anisotropy is zero for an isolated free atom). We note that a straightforward extension of the basis set does not solve the problem of BSSE as δ^{BSSE} may increase with the size of the basis set.

For He we use a [10s4p2d/6s4p2d] basis, with 6 Cartesian d functions. The s orbitals are taken from Ref. [13] and the 3p2d set from Ref. [14]. For a more accurate description of the shielding we have added a tight p function with the exponent derived using a geometric progression.

For Ar and Na⁺ the initial s and p basis sets are taken from Partridge [15]. We have added to the 17s12p Ar and 15s10p Na⁺ sets diffuse s and p functions (using geometric progression for the exponents) and spherical d and f ANO-type functions [16]. Our final basis is 18s13p4d3f for Ar and 17s12p3d2f for Na⁺.

In all the calculations, gauge invariant atomic orbitals (GIAO’s, London orbitals) are used (see

Refs. [17,18] for details of the formulation we apply). Since in these calculations $\delta(R)$ values are small and the internuclear distances large, it is essential to make sure the results are gauge origin independent. All calculations have been carried out using the Hermit–Sirius–Abacus program system¹.

The accuracy of the basis sets can be estimated by comparing the computed atomic properties with literature results. For the shielding, we obtain (recalling that we discuss full-CI values for He and SCF results for Ar and Na⁺) $\sigma_{\text{He}} = 59.89462241$, $\sigma_{\text{Ar}} = 1237.65675689$ and $\sigma_{\text{Na}^+} = 623.81649396$ ppm. The SCF results are reproduced exactly to eight decimal places in the Ar and Na⁺ calculations with a ghost basis set. For He–ghost at the largest interatomic distance studied, the difference (due to numerical accuracy problems) does not exceed 3×10^{-6} ppm and can be neglected. To estimate the asymptotic behaviour of the shielding anisotropy the magnetizabilities of the isolated atoms are required. We find $\chi_{\text{He}} = -0.3990$, $\chi_{\text{Ar}} = -4.3396$ and $\chi_{\text{Na}^+} = -1.0689$ au. The conversion factor for the comparison with $\Delta\sigma$ in ppm is $-3c^{-2} = -3 \times 53.25$, since the asymptotic value of the R^{-3} coefficient is -3χ . We have also computed the values of B for He and Ar, which are 39.78 and 1243.81, respectively.

These results for the isolated atoms, full-CI for He and SCF for Ar and Na⁺, are in good agreement with available literature data (see e.g. Refs. [19–21]). As we compare our own values from the supermolecular calculation with our own values for the free atoms, we do not need to reproduce the best results exactly. For example, we cannot and need not use basis sets as large as in other works where only single atoms have been studied.

For the He dimer, we may compare our results for the energies (CP corrected) with other calculations. We find the minimum of the interaction potential at $R = 5.68$ au and that the depth of the minimum is

¹ T. Helgaker, P.R. Taylor, K. Ruud, O. Vahtras and H. Koch, HERMIT, a molecular integral program. H.J.Aa. Jensen and H. Ågren, SIRIUS, a program for calculation of MCSCF wavefunctions. T. Helgaker, K.L. Bak, H.J.Aa. Jensen, P. Jørgensen, R. Kobayashi, H. Koch, K. Mikkelsen, J. Olsen, K. Ruud, P.R. Taylor and O. Vahtras, ABACUS, a second-order MCSCF molecular property program.

3.06×10^{-5} au. A fit to the long range part of the computed potential using R^{-6} and R^{-8} gives $C_6 = 1.461$ and $C_8 = 14.77$. These numbers are in good agreement with accurate ab initio results, e.g. the corresponding values given most recently are $R_{\min} = 5.6165$ au, depth 3.4789×10^{-5} au, $C_6 = 1.461$ and $C_8 = 14.11$ [22] (see also Ref. [23]). Since we are interested here in the shielding and not in the energies, we did not attempt to extend the basis set, compute more points near the minimum or improve the calculated potential curve in any way.

For the analysis of the shielding in He–He we have chosen the range of $R \geq 5.0$ au and included 5.6 au in order to have an idea of the behaviour at the van der Waals minimum. For Ar–Na⁺, we have chosen the R values starting from 4.0 au, where $\delta(R)$ is large enough to be of experimental interest. We find the minimum at $R = 5.53$ au, in good agreement with other results [24].

3.1. Long range effects on the anisotropy

Our main results showing the effects of the interaction on the shielding are given in Tables 1–3. We start the discussion of the results with the anisotropy. It appears rather unlikely that a reliable description of the R^{-4} or R^{-6} dependence of $\delta(R)$ can be obtained without prior proper description of the R^{-3}

dependence expected for the anisotropy. An analysis of the results for $\Delta\sigma$ should indicate how reliable results are to be expected for $\delta(R)$, and also tell us in what region any R^{-n} expansion can be sufficiently accurate.

The long range dependence of the incremental anisotropy $\Delta\sigma$ is well reproduced by the expression $-3\chi/R^3$. In particular, for $\Delta\sigma_{\text{He}}$ the agreement is good, as shown in Table 1. We cannot neglect the basis set superposition effects, the convergence is clearly better when the results are counterpoise corrected. For $\Delta\sigma_{\text{Ar}}$, the convergence to $-3\chi_{\text{Na}^+}$ is very slow, and apparently the BSSE is too large to obtain reliable results in the region $R = 14$ – 20 au even with the appropriate correction. Finally, for $\Delta\sigma_{\text{Na}^+}$ the results converge well to $-3\chi_{\text{Ar}}$, and as for He the CP correction leads to smoother convergence.

3.2. Long-range effects on the isotropic shielding

In the He–He interaction, we have obtained a reasonably stable value of δR^6 in the range $7.5 \leq R \leq 12$ au (where the values of $\delta(R)$ change by a factor of 20). For larger R , $\delta(R)$ becomes smaller and R^6 very large and we consequently lose accuracy in the results. A better fit to $\delta(R)$ is obtained using two parameters, R^{-6} and R^{-8} . Such a fit

Table 1
Long-range effects on the shielding of He in He–He interaction^a

R	$\Delta\sigma$	$\Delta\sigma^{\text{BSSE}}$	$\Delta\sigma R^3$	δ	δ^{BSSE}	δR^6
5.0	0.51913167	0.00014619	64.89	-0.00269019	-0.00024540	-42.0
5.6	0.36533156	0.00026878	64.16	-0.00169951	-0.00026045	-52.4
6.0	0.29607333	0.00027125	63.95	-0.00128450	-0.00024030	-59.9
6.5	0.23244685	0.00021477	63.84	-0.00088794	-0.00019623	-67.0
7.0	0.18596677	0.00013678	63.79	-0.00059954	-0.00014525	-70.5
7.5	0.15114323	0.00006535	63.76	-0.00039908	-0.00010046	-71.0
8.0	0.12451580	0.00001852	63.75	-0.00026864	-0.00006409	-70.4
8.5	0.10379894	-0.00000229	63.75	-0.00018316	-0.00004054	-69.1
9.0	0.08743760	-0.00000752	63.74	-0.00012667	-0.00002641	-67.3
10.0	0.06373957	-0.00000319	63.74	-0.00006524	-0.00001003	-65.2
11.0	0.04788812	-0.00000047	63.74	-0.00003583	-0.00000355	-63.5
12.0	0.03688575	-0.00000004	63.74	-0.00002095	-0.00000161	-62.6
15.0	0.01888516	0.00000000	63.74	-0.00000502	-0.00000154	-57.1
∞^b			63.74			

^a R in au, $\Delta\sigma$, $\Delta\sigma^{\text{BSSE}}$, δ and δ^{BSSE} in ppm. ^b Estimated from $-3\chi_{\text{He}}$.

Table 2
Long-range effects on the shielding of Ar in Ar–Na⁺ interaction^a

R	$\Delta\sigma$	$\Delta\sigma^{\text{BSSE}}$	$\Delta\sigma R^3$	δ	δ^{BSSE}	δR^4
4.0	32.66541045	-0.03534156	2090.59	-20.00612259	0.02326084	-5121.6
5.0	10.14942361	-0.03702199	1268.68	-6.01060368	0.02473546	-3756.6
6.0	4.67975953	-0.02195822	1010.83	-2.71019613	0.01493098	-3512.4
7.0	2.38244700	-0.01456488	817.18	-1.33110238	0.01002844	-3196.0
8.0	1.24664941	-0.01327481	638.28	-0.65626763	0.00900956	-2688.1
9.0	0.66639403	0.00522854	485.80	-0.31968797	-0.00347857	-2097.5
10.0	0.37841416	0.01548811	378.41	-0.16047048	-0.01039662	-1604.7
11.0	0.25011662	0.01144509	332.91	-0.09721228	-0.00771593	-1423.3
12.0	0.18741379	0.00523539	323.85	-0.07105157	-0.00356121	-1473.3
13.0	0.13857760	-0.00014303	304.46	-0.04978885	0.00004433	-1422.0
14.0	0.09528926	-0.00551947	261.47	-0.02928426	0.00364266	-1125.0
15.0	0.06559183	-0.00803830	221.37	-0.01579421	0.00533205	-799.6
16.0	0.05029112	-0.00638017	205.99	-0.01044439	0.00423585	-684.5
18.0	0.03852013	-0.00059379	224.65	-0.00939332	-0.00039103	-986.1
20.0	0.02980252	0.00053314	238.42	-0.00795412	-0.00035620	-1272.7
22.0	-0.02202529	-0.00017738	234.53	-0.00570766	-0.00011833	-1337.1
26.0	0.01255259	0.00000231	220.62	-0.00290787	-0.00000154	-1328.8
30.0	0.00776622	0.00000000	209.69	-0.00161202	0.00000000	-1305.7
35.0	0.00466492	0.00000000	200.01	-0.00085827	0.00000000	-1287.9
40.0	0.00301559	0.00000000	193.00	-0.00049874	0.00000000	-1276.8
50.0	0.00146775	0.00000000	183.47	-0.00020223	0.00000000	-1263.9
70.0	0.00050400	0.00000000	172.87	-0.00005214	0.00000000	-1251.9
100.0	0.00016504	0.00000000	165.04	-0.00001242	0.00000000	-1241.7
∞^b			170.76			

^a R in au, $\Delta\sigma$, $\Delta\sigma^{\text{BSSE}}$, δ and δ^{BSSE} in ppm. ^b Estimated from $-3\chi_{\text{Na}^+}$.

Table 3
Long-range effects on the shielding of Na⁺ in Ar–Na⁺ interaction^a

R	$\Delta\sigma$	$\Delta\sigma^{\text{BSSE}}$	$\Delta\sigma R^3$	δ	δ^{BSSE}
4.0	78.98264027	0.00342013	5054.89	-45.27007427	-0.00229738
5.0	21.38085845	0.00239533	2672.61	-10.40679798	-0.00184903
6.0	6.52605775	0.00202425	1409.63	-2.14042934	-0.00147655
7.0	2.65907427	0.00130643	912.06	-0.39575729	-0.00091946
8.0	1.47457752	0.00070063	754.98	-0.06773120	-0.00044103
9.0	0.97608183	0.00053839	711.56	-0.01088551	-0.00030901
10.0	0.69987974	-0.00020334	699.88	-0.00145872	0.00017196
11.0	0.52328840	-0.00072321	696.50	-0.00001295	0.00050237
12.0	0.40240224	-0.00076619	695.35	0.00012442	0.00052142
13.0	0.31626153	-0.00055535	694.83	0.00009115	0.00037545
14.0	0.25308168	-0.00030822	694.46	0.00006833	0.00020786
15.0	0.20567511	-0.00013579	694.15	0.00005877	0.00009163
16.0	0.16941697	-0.00004872	693.93	0.00004935	0.00003303
18.0	0.11894456	-0.00000370	693.68	0.00002911	0.00000259
20.0	0.08669252	-0.00000015	693.54	0.00001779	0.00000012
22.0	0.06512265	-0.00000001	693.43	0.00001286	0.00000001
26.0	0.03944631	0.00000000	693.31	0.00000680	0.00000000
30.0	0.02567582	0.00000000	693.25	0.00000406	0.00000000
35.0	0.01616821	0.00000000	693.21	0.00000228	0.00000000
40.0	0.01083122	0.00000000	693.20	0.00000138	0.00000000
50.0	0.00554555	0.00000000	693.19	0.00000058	0.00000000
∞^b			693.25		

^a R in au, $\Delta\sigma$, $\Delta\sigma^{\text{BSSE}}$, δ and δ^{BSSE} in ppm. For a discussion of $\delta(R)$ see the text. ^b Estimated from $-3\chi_{\text{Ar}}$.

gives -55 for the R^{-6} coefficient. This value is still somewhat larger than expected from the simple estimate (6), $-BC_6/\alpha$ is ≈ -42 . It remains to be seen how accurate this estimate is, in particular how $B(-i\omega; i\omega, 0, 0)$ depends on $i\omega$.

The dependence of δ_{Ar} on interatomic distance is shown in Table 2. In the region where δ^{BSE} is too large ($R = 14.0$ – 20.0 au) the convergence pattern breaks down. Similarly to $\Delta\sigma_{Ar}$, the accuracy of the results appears to be lower in this region. However, it is evident that for very large values of R we obtain an R^{-4} dependence, and a two parameter fit (R^{-4} and R^{-6}) gives -1238 as the first coefficient. This value is in excellent agreement with our $B_{Ar} = 1243.81$.

For δ_{Na^+} the expected R^{-6} dependence resulting from the dispersion interaction cannot be reproduced within the SCF approach. We observe at long range an asymptotic R^{-4} dependence, with a very small coefficient (≈ 3.6). We attribute it to an artefact of the calculation, namely errors due to incompleteness of the basis set. According to Hansen and Bouman [11], various terms asymptotically dependent on R^{-2} should cancel out, but it does not happen for incomplete basis sets. Apparently, for spherically symmetric interacting systems the first such terms arise for R^{-4} , and in the absence of other nonzero contributions this is what we observe.

4. Conclusions

We have studied the effect of the long-range interaction on the shielding in atom–atom and atom–ion systems. The results obtained from supermolecular calculations exhibit the expected asymptotic convergence behaviour. The R^{-n} expansion coefficients compare favourably with values derived when the interatomic interaction is treated as a perturbation. However, the simplest formulas expressing $\delta(R)$ using one-term expansions are valid only for large interatomic distances and small values of $\delta(R)$. At least two terms in the R^{-n} expansion must be used to reproduce the calculated results for smaller R . For example, for δ_{Ar} ($R = 4.0$) we obtain -5.2 ppm from the asymptotic formula using only the R^{-4} term, whereas a two-term expansion yields -19.3

ppm, in good agreement with the value calculated for the $Ar-Na^+$ supermolecule, -20.0 ppm.

From the experimental point of view, it is more interesting to consider the results at smaller interatomic distances. The supermolecular calculations are simpler for this region because the effect of the interaction is large and one can neglect the basis set superposition errors. On the other hand, the interpretation of the results is more difficult since one cannot treat the interaction as a weak perturbation.

For the interaction of neutral rare gas atoms there is a significant difference between the region of small interatomic distances and the asymptotic region of large R . In the first, as shown by Jameson and de Dios [5,6] for the $Ar-Ar$ interaction, large values of $\delta(R)$ are obtained at the SCF level (we obtained similar results for $Ar-Ar$ in test SCF calculations). The dispersion effects are not accounted for at the SCF level of approximation for the energies and are thus absent when a version of the Hartree–Fock perturbation approach is used to calculate the shielding. This suggests that $\delta(R)$ is mainly due to overlap and exchange effects and it may be appropriate to assume for this region an exponential decrease of $\delta(R)$ typical for these effects. It has been noticed previously [25] that one should not attribute effects observed in SCF-type calculations to dispersion.

On the other hand, in the region of large internuclear distances the effects vanishing as R^{-n} will be dominant. The idea underlying the derivation of R^{-n} expansion coefficients by Jameson and de Dios [5,6] and our Eq. (6) was to account for dispersion effects, and these are automatically taken care of in supermolecular calculations that include correlation. For large R it is hence appropriate to describe $\delta(R)$ using a fit of the form R^{-n} with the coefficients related to C_n .

In the case of atom–ion interactions, the SCF approximation is capable of describing the dominant induction terms. However, for a given atom interacting with various ions in the range where $\delta(R)$ can be expressed by the asymptotic formula using the R^{-4} term, the effect should depend only on the charge of the ion. Apparently, this is not so for the Xe -ion systems considered by Freitag et al. [8], where δ_{Xe} behaves in a different way for each singly positive ion. One possibility is that in this case the short-range overlap and exchange effects cannot

be neglected. Another possible explanation is that just as in our Ar–Na⁺ calculations, at least two terms of the long-range asymptotic expansion of $\delta(R)$ should be included in the region of interatomic distances where $\delta(R)$ is large.

Finally, as there are numerous recent studies of shielding polarizabilities (see e.g. Refs. [7,26] and a review [27]), we want to point out that the shielding polarizabilities are more useful than it may appear from this work. In the case of molecule–molecule interactions the effects on the shielding are different from those analysed here. They are much larger because of lower symmetry, nonzero multipole moments and nonzero susceptibilities of the interacting subsystems, and they may presumably be well described using asymptotic formulas derived from appropriate long-range perturbation expansions.

Acknowledgement

A significant part of the calculations described in this work has been performed at the University of Aarhus. We are obliged to Dr. P. Jørgensen for his support, permission to use the computer time, as well as for reading and commenting on the manuscript. We acknowledge many helpful discussions with Dr. G. Chałasiński, Dr. B. Jeziorski and Dr. R. Moszyński. Finally, helpful comments of Professor Dr. A.D. Buckingham are gratefully acknowledged. This work has received support from the Norwegian Supercomputing Committee (TRU) through a grant of computer time.

References

- [1] [A.D. Buckingham and K.L. Clarke, *Chem. Phys. Letters* 57 (1978) 321.
- [2] [K.L.C. Hunt, B.A. Zilles and J.E. Bohr, *J. Chem. Phys.* 75 (1981) 3079.
- [3] [M. Jaszuński, *Chem. Phys. Letters* 135 (1987) 565.
- [4] [P.W. Fowler, K.L.C. Hunt, H.M. Kelly and A.J. Sadlej, *J. Chem. Phys.* 100 (1994) 2932.
- [5] [C.J. Jameson and A.C. de Dios, *J. Chem. Phys.* 97 (1992) 417.
- [6] [C.J. Jameson and A.C. de Dios, *J. Chem. Phys.* 98 (1993) 2208.
- [7] [M. Grayson and W.T. Raynes, *Magn. Res. Chem.* 33 (1995) 138.
- [8] [A. Freitag, Ch. van Wullen and V. Staemmler, *Chem. Phys.* 192 (1995) 267.
- [9] [C.J. Jameson and A.C. de Dios, in: *Nuclear magnetic shielding and molecular structure*, NATO ASI Series C, Vol. 386, ed. J.A. Tossell (Kluwer, Dordrecht, 1993).
- [10] [G. Chałasiński and M.M. Szcześniak, *Chem. Rev.* 94 (1994) 1723.
- [11] [Aa.E. Hansen and T.D. Bouman, *J. Chem. Phys.* 82 (1985) 5035.
- [12] [H.M. McConnell, *J. Chem. Phys.* 27 (1957) 226.
- [13] [F.B. van Duijneveldt, *IBM Res. J.* (1971) 945.
- [14] [M. Gutowski, J. Verbeek, J.H. van Lenthe and C. Chałasiński, *Chem. Phys.* 111 (1987) 271.
- [15] [H. Partridge, *J. Chem. Phys.* 87 (1987) 6643; NASA Technical Memorandum 89449.
- [16] [P.-O. Widmark, B.J. Persson and B.O. Ross, *Theoret. Chim. Acta* 79 (1991) 419.
- [17] [T. Helgaker and P. Jørgensen, *J. Chem. Phys.* 95 (1991) 2595.
- [18] [J. Olsen, K.L. Bak, K. Ruud, T. Helgaker and P. Jørgensen *Theoret. Chim. Acta* 90 (1995) 421.
- [19] [D.M. Bishop and S.M. Cybulski, *Chem. Phys. Letters* 211 (1993) 255.
- [20] [D.M. Bishop and S.M. Cybulski, *J. Magn. Reson. A* 107 (1994) 99.
- [21] [G. Malli and S. Fraga, *Theoret. Chim. Acta* 5 (1966) 275.
- [22] [K.T. Tang, J.P. Toennies and C.L. Liu, *Phys. Rev. Letters* 74, (1995) 1546.
- [23] [B. Jeziorski, R. Moszyński and K. Szalewicz, *Chem. Rev.* 94 (1994) 1887.
- [24] [R. Ahlrichs, J. Böhm, S. Brode, K.T. Tang and J.P. Toennies, *J. Chem. Phys.* 88 (1988) 6290.
- [25] [A.C. de Dios and E. Oldfield, *J. Am. Chem. Soc.* 116 (1994) 7453.
- [26] [A. Rizzo, T. Helgaker, K. Ruud, A. Barszczewicz, M. Jaszuński and P. Jørgensen, *J. Chem. Phys.* 102 (1995) 8953.
- [27] [W.T. Raynes, in: *Encyclopedia of NMR*, eds. D.M. Grant and R.K. Harris (Wiley, New York), in press.