_3_ IMPROVEMENT OF UNCOUPLED HARTREE FOCK EXPECTATION VALUES

FOR PHYSICAL PROPERTIES, II.* _6_

by

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ABSTRACT

A comparison is made between approximate polarizabilities
calculated in the coupled Hartree-Fock approximation with those
obtained from the uncoupled Hartree-Fock approximation with first
order corrections.

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In a previous paper[1] under this title formulae have been given

for the first order corrections to the uncoupled Hartree-

Fock[2,3] approximation for atomic properties[4,5]. Recently Langhoff

et. al.[6] compared the various Hartree-Fock perturbation schemes for

second order properties. Using their first order wave functions,

kindly supplied to us by Prof. R. P. Hurst, we have evaluated the

corrections to the dipole and quadrupole polarizabilities of various

atoms and ions. The results[7] are given in Tables I and II. Also

included are values calculated in the coupled Hartree-Fock

approximation[6], and accurate values where available. We would now

like to make some comment on various aspects of these results.

(i) The uncoupled polarizability plus first order correction

is seen in every case to be less than the coupled polarizability[9].

Actually it is straight forward to show that this is true quite

generally. Let $\mathcal{H}$ be the total Hamiltonian, including the external

field, let Φ be the uncoupled Hartree-Fock wave function and ψ'

the coupled Hartree-Fock wave function, all defined in reference 1 .

Since both Φ and ψ' are single determinants, it follows that

$$\langle \Phi | \mathcal{H} | \Phi \rangle \geq \langle \psi' | \mathcal{H} | \psi' \rangle \qquad (1)$$

as ψ' is, by definition, the energy optimized single determinant.

We now imagine expanding both sides in powers of the external field.

As Φ and ψ' are equal at zero field, one readily verifies that

the zero and first order terms in the expansion of Eq. (1) are equal.

Thus, if we now let the field go to zero, we get a corresponding inequality for the second order energies. This then is the announced inequality[10]. Namely, by definition the quantity on the right is minus one half times the coupled polarizability, and one readily sees, using the results of reference 1, that the quantity on the left is minus one half the uncoupled polarizability plus first order correction.

(ii) For some of the cases listed, the corrected uncoupled values for the polarizabilities differ significantly[11] from those calculated in the coupled approximation. Since the latter are well known[2] to be correct "through first-order", this serves to emphasize the point already made in Ref. 1 - that being accurate through first-order in the uncoupled Hartree-Fock approximation is not the same as being correct through first order in the coupled approximation.

(iii) To investigate further the relative accuracy of the two approximations, we have calculated the second order correction to the uncoupled Hartree-Fock electron dipole polarizability for one electron systems. In this case the coupled theory is exact. The results given in Table III indicate that the convergence is slow, except, of course, for larger z[11].

(iv) The hope expressed in reference 1, that the uncoupled second order properties with first order corrections might have an accuracy comparable to the coupled result, does not seem to be borne out for near neutral systems.

ACKNOWLEDGEMENT

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Footnotes

1. D. F. Tuan, S. T. Epstein, and J. O. Hirschfelder, J. Chem. Phys. $\underline{44}$, 431 (1966).

2. A. Dalgarno, Proc. Roy. Soc. (London) $\underline{A251}$, 282 (1959).

3. Our discussion in this paper is limited to Dalgarno's uncoupled Hartree-Fock approximation (approximation "C" of Langhoff et al[6].).

4. The corrections apply to closed shell systems or to the open shell case if the initial wave function is an unrestricted Hartree-Fock wave function.

5. It perhaps should be pointed out that the first order corrections to properties bilinear in perturbation parameters, e.g. shielding factors and chemical shifts, can be obtained by replacing μW in reference 1, with $\mu_1 W_1 + \mu_2 W_2$ and examining the cross terms in Eqs. (30) and (31) of that paper. It can be seen that first order wavefunctions in <u>both</u> perturbations are needed to obtain the correction.

6. P. W. Langhoff, M. Karplus and R. P. Hurst, J. Chem. Phys. $\underline{44}$, 505 (1966).

7. For the 3-electron problem Langhoff et.al.[6] used restricted wave functions as the zero-order Hartree-Fock orbitals. It is felt, since the inner shell electrons contribute less than a percent of the total polarizability and since the 2s orbital changes only slightly in going from the restricted calculation

Footnotes (continued)

to the unrestricted[8], that the quoted results will be good
approximations to the unrestricted polarizabilities.[4]

8. L. M. Sachs, Phys. Rev. <u>117</u>, 1504 (1960).

9. It appears from comparison with the available accurate data
listed in Table I, that the coupled polarizability is less than
the exact result. See also, A. Dalgarno and J. M. McNamee,
Proc. Phys. Soc. (London) <u>77</u>, 673 (1961).

10. This inequality holds even if approximate first order wave
functions are used if they are obtained from a variational
calculation using the same basis set in the two cases, as is
done by Langhoff et. al.[6].

11. As the nuclear charge becomes large compared to the number of
electrons the two approximations become, of course, quite
comparable as the electron-electron interaction becomes a small
correction.

Table I. Dipole Polarizabilities, $\alpha_d (\mathring{A}^3)$.

Atom or Ion	Uncoupled[a]			Coupled[a]	Accurate
	α_0	α_1	$\alpha_0 + \alpha_1$	α_0	α
He	0.148	0.036	0.184	0.196	0.2051 [b]
Li	0.234×10^{-1}	0.039×10^{-1}	0.273×10^{-1}	0.281×10^{-1}	0.2852×10^{-1} [b]
Be^{2+}	0.671×10^{-2}	0.086×10^{-2}	0.757×10^{-2}	0.769×10^{-2}	0.7×10^{-2} [c]
B^{3+}	0.260×10^{-2}	0.026×10^{-2}	0.286×10^{-2}	0.290×10^{-2}	0.33×10^{-2} [c]
C^{4+}	0.121×10^{-2}	0.010×10^{-2}	0.131×10^{-2}	0.132×10^{-2}	0.15×10^{-2} [c]
N^{5+}	0.638×10^{-3}	0.047×10^{-3}	0.685×10^{-3}	0.688×10^{-3}	
Li	7.51	4.67	12.18	21.7	22 ± 2 [d], 24.4 ± 2.4 [f]
Be^+	1.20	0.59	1.79	2.53	
B^{2+}	0.371	0.154	0.525	0.660	
C^{3+}	0.153	0.055	0.208	0.246	
N^{4+}	0.750×10^{-1}	0.238×10^{-1}	0.988×10^{-1}	0.113	
O^{5+}	0.411×10^{-1}	0.117×10^{-1}	0.528×10^{-1}	0.583×10^{-1}	
Be	4.28	1.26	5.54	6.26	
B^+	1.07	0.24	1.31	1.40	
C^{2+}	0.398	0.073	0.471	0.496	
N^{3+}	0.184	0.029	0.213	0.221	
O^{4+}	0.976×10^{-1}	0.135×10^{-1}	0.111	0.114	
F^{5+}	0.566×10^{-1}	0.070×10^{-1}	0.636×10^{-1}	0.650×10^{-1}	

a The qualities α_0 and α_1 are the zero-order approximation and
first order correction to the polarizabilities
comparable to quantities $\langle Q \rangle_0$ and $\langle Q \rangle_1$ of reference 1 .

Table I. Dipole Polarizabilities,   (cont'd)

b   K. T. Chung and R. P. Hurst, Phys. Rev., 152, 35 (1966)
    (Accurate calculation).

c   J. E. Meyer and M. G. Hayes, Phys. Rev. 43, 605 (1933).
    (Spectroscopic interpretation).

d   G. E. Chamberlain and J. C. Zorn, Phys. Rev. 129, 677 (1963),
    (Atomic beam).

f   A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) A73,
    455 (1959). (Calculated from theoretical oscillator strengths).

g   For 3-electron systems see footnote 7.

Table II. Quadrupole Polarizabilities, α_Q (Å^5).

Atom on Ion	Uncoupled [a]			Coupled [a]
	α_0	α_1	$\alpha_0 + \alpha_1$	α
He	0.748×10^{-1}	0.169×10^{-1}	0.917×10^{-1}	0.967×10^{-1}
Li$^+$	0.397×10^{-2}	0.059×10^{-2}	0.456×10^{-2}	0.466×10^{-2}
Be^{2+}	0.567×10^{-3}	0.063×10^{-3}	0.630×10^{-3}	0.638×10^{-3}
B^{3+}	0.130×10^{-3}	0.011×10^{-3}	0.141×10^{-3}	0.143×10^{-3}
C^{4+}	0.399×10^{-4}	0.029×10^{-4}	0.428×10^{-4}	0.431×10^{-4}
N^{5+}	0.149×10^{-4}	0.009×10^{-4}	0.158×10^{-4}	0.159×10^{-4}
Li [b]	32.3	15.4	47.7	62.0
Be$^+$	1.51	0.52	2.03	2.31
B^{2+}	0.218	0.059	0.277	0.300
C^{3+}	0.519×10^{-1}	0.117×10^{-1}	0.636×10^{-1}	0.671×10^{-1}
N^{4+}	0.165×10^{-1}	0.032×10^{-1}	0.197×10^{-1}	0.204×10^{-1}
O^{5+}	0.632×10^{-2}	0.107×10^{-2}	0.739×10^{-1}	0.761×10^{-2}
Be	9.23	3.29	12.5	14.4
B$^+$	0.880	0.233	1.11	1.20
C^{2+}	0.171	0.036	0.207	0.217
N^{3+}	0.488×10^{-1}	0.087×10^{-1}	0.575×10^{-1}	0.593×10^{-1}
O^{4+}	0.175×10^{-1}	0.027×10^{-1}	0.202×10^{-1}	0.207×10^{-1}
F^{5+}	0.733×10^{-2}	0.099×10^{-2}	0.832×10^{-2}	0.847×10^{-2}

a. The quantities α_0 and α_1 are the zero-order approximation and first order correction to the polarizabilities, comparable to quantities $\langle Q \rangle_0$ and $\langle Q \rangle_1$ of reference 1.

b. For the 3-electron system see footnote 7.

Table III. Dipole Polarizabilities for the One Electron Atom
and Ions in the Uncoupled Hartree-Fock Approximation,*
(Atomic Units).

Z	$Z^4 \times \alpha_0$	$Z^4 \times \alpha_1$	$Z^4 \times \alpha_2$	$Z^4 \times (\alpha_0 + \alpha_1 + \alpha_2)$
1	2.559	1.103	.476	4.138
2	3.263	.897	.247	4.407
3	3.592	.725	.146	4.463
4	3.783	.603	.096	4.482
5	3.907	.515	.067	4.489
6	3.995	.448	.050	4.493

* The coupled theory is exact with $\alpha (a.u.) = 4.5/Z^4$ for all
values of the nuclear-charge Z . The quantities α_0 , α_1 and α_2
are the zero-order approximation and the first two corrections to
the polarizability, comparable to $\langle Q \rangle_0$, $\langle Q \rangle_1$,
and $\langle Q \rangle_2$ of reference 1.