Finite-Field Hartree-Fock Calculations of Atomic and Molecular Polarizabilities

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Abstract   The experiment of calculating atomic and molecular dipole polarizabilities within the Hartree-Fock approximation in the finite-field scheme is described. Small system (Li, Li^-, Li_2, Li_2^+, Be) are selected to facilitate the use of extended basis sets. For Li- a very extensive set including a large number of diffuse and polarization functions is required to achieve a stable value, Thé results are compared with other theoretical and experimental da-ta and are possibly within the accuracy of the Hartree-Fock model. The remaining error is essentially isolated as the correlation error. Inclusion of correlation corrections is discussed and postponed to a later stage.

1. INTRODUCTION

An atom or molecule subjected to an external electric field suffers a perturbation which induces electric moments. The response of the system to such an external perturbation is primarily linear for relatively small field intensities and is given by the dipole polarizability[1].

Experimentally, polarizabilities can be determined by several techniques such as optical interferometry[2], field emission[3], index of refraction[4], Stark effect[5], spectral oscillator-strength measurements[6], dielectric constant[7] etc, to mention a few. In practice, they are relatively difficult to obtain and discrepancies do exist even for simple atoms[8]. Theoretically, the calculation of polarizabilities is known to depend on details of the wavefunction that may be difficult to uncover[9]. Results at the Hartree-Fock (HF) level are in error by 3 to 12%[10]. Formally, the calculation of polarizabilities may be performed within the framework of perturbation theory where the polarizability is related to the second-order correction to the energy of the system perturbed

by the electric field[11]. The main problem is, of course, that one does not even know the exact unperturbed solution for the many-electron system. Instead, in the finite-field approach[12] the calculations are performed for the field-dependent problem. The resulting wavefunction and energy are consequently field-dependent and one may obtain the polarizability directly by differentiating the energy with respect to the field, thereby avoiding a perturbative treatrnent.

In this paper such a procedure is used to calculate the static (frequency-independent) dipole polarizabilities of some simple systerns (Li, Li$^-$, Li$_2$, Li$_2^+$ and Be) within the framework of the HF approximation. Correlation effects, neglected by the HF procedure, are not considered; not because they are unimportant but rather because the HF test should be taken before correlation is introduced. The systematic study of polarizabilities for some simple systems is part of our project. The main purpose of this paper is therefore to report on our experience at the first and simpler step where correlation contributions are not included. A specific computer program has been written towards this end, such that it allows subsequent corrections due to correlation. In the next sections we briefly describe how the polarizabilities are calculated. Then we present our results and compare them with other theoretical and experimental data. In a final section we discuss the sources of errors in the calculations, together with our conclusions and perspective.

2. NONPERTURBATIVE APPROACH TO POLARIZABILITIES

The perturbed energy due to the application of a static electric field of strength λ may be given by the perturbation series.

$$E_0(\lambda) = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \lambda^3 E_0^{(3)} + \ldots$$

Even though this series is generally asyrnptotically divergent, to each of its terrn may be given a physical significance. The first-order term is the permanent dipole moment μ_0:

$$E_0^{(1)} = <\psi_0^{(0)}|V|\psi_0^{(0)}> = \mu_0 \; ;$$

the second-order term is related to the static dipole polarizability a:

$$E_0^{(2)} = <\psi_0^{(0)}|V|\psi_0^{(1)}> = \sum_{n\neq 0} \frac{|<\psi_0^{(0)}|V|\psi_n^{(0)}>|^2}{E_0^{(0)} - E_n^{(0)}} = -\frac{1}{2}\alpha_0 \quad ;$$

and higher-order te-ms are related to the hyper polarizabilities. The notation in the above equations is standard. The major drawback with this approach is that the unperturbed solutionr $\psi_n^{(0)}$ and $E_n^{(0)}$ are not exact but obtained in some approximation, A non-perturbative treatment is possible, as it follows from the equations above that

$$\mu_0 = E_0^{(1)} = \frac{\partial E(\lambda)}{\partial \lambda}\bigg|_{\lambda=0}$$

and

$$\alpha_0 = -2E_0^{(0)} = -\frac{\partial^2 E(\lambda)}{\partial\lambda^2}\bigg|_{\lambda=0}$$

therefore the electric properties are directly related to the field-dependent energy $E(\lambda)$ and the series expansion may be avoided by a direct computation of $E(\lambda)$. The major advantage of this approach is that the polarizability may be obtained from standard computer programs for the calculation of total energies, just by adding to the original hamiltonian the additional terms due to the perturbation. The major disadvantage follows from the possible inaccuracies of the numerical differentiation. Utilizing the HF method (or rather SCF, in a finite basis expansion) there is a simple way to check on the numerical accuracy. This follows if one also calculates the dipole moment. In the field-dependent case this is given by

$$\mu(\lambda) = \mu_0 - \lambda\alpha + \dots$$

and therefore.,

$$\mu_0 = \mu(0)$$

and

$$\alpha = -\frac{\partial\mu(\lambda)}{\partial\lambda}\bigg|_{\lambda=0}$$

Hence the polarizability may be obtained also from the first derivative of $\mu(\lambda)$.

In the present paper both ways are utilized to compute a and this allows one to check on the numerical differentiation, as discussed below.

3. DETAILS OF THE CALCULATIONS

All calculations have been performed at the HF level utilizing the spin-unrestricted HF (UHF) wavefunction. Starting from a conventional UHF program additional routines are required and were written: i) inclusion of the electric field term in the hamiltonian to obtain the field-dependent self-consistency; ii) calculation of the dipole moment from the computed self-consistent wavefunctions; and iii) as we are using a UHF approach for the open shell cases, the wavefunctions are not necessarily eigenfunctions of the spin operator S^2 as they should; so, to check on the spin contamination an additional subroutine calculates $<S^2>_{UHF}$. In all cases reported here the spin contaminations are actually negligible. The only open-shell calculations are performed for Li and Li,$^+$ In these cases $<S^2>_{UHF} = 0.750$ thus reproducing the exact result. The program is rather general[13] and both the energy and dipole moment may be calculated after specifying the three cartesian components of the electric field. Of course, higher moments such as the quadrupole moment may also be calculated but at this stage no attempt has been made to do this,

The HF calculations are made by utilizing the so-called algebraic approximation in which the one-particle states are expanded in a finite set of atomic functions. This leads to the SCF approximation to the HF theory. Most inaccuracies of the SCF calculations may be traced to the inadequacy of the chosen basis sets[10]. For polarizability calculations, where one is essentially calculating the change of the electronic distribution due to the electric field, the inclusion of diffuse functions in the basis set is known to be very important[10,14,15]. Specific basis functions taking into account the distortion of the electronic charge by the external field are possible within the electric -field variant[15] basis set. Here we decided to adopt the simple standard basis sets, augmented by diffuse and polarization functions.

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For the Li atom we started from the suggestion by Gianolio et $al.$[16] of the $9s$ contracted to $4s$ gaussian functions and augmented with polarization p functions, and to the final set we added diffuse s and p functions. The complete set is now a $(10s5p)$ contracted to $(5s3p)$, giving a total SCF energy of $-7.43217h$ as compared to the exact HF value of $-7.43273h$ [17]. This is the basis utilized for all calculations involving Li, except Li⁻. In this case we have proceeded (see below) to increase this $(10s5p|5s3p)$ basis set to the very extended $(15s8p|10s6p)$ basis set.

For Be we have used the suggestion of ref.18 and augmented this basis with diffuse s and p functions. The final set consists of $(10s5p|6s3p)$ and gives a total SCF energy of $-14.57233h$.

Having obtained both the field-independent and the field-dependent energy and dipole moment, the first and second derivatives were then calculated in the finite difference approximation:

$$\frac{\partial E(\lambda)}{\partial \lambda}\bigg|_{\lambda=0} = \frac{E(\lambda_0)-E(-\lambda_0)}{2\lambda_0}$$

$$\frac{\partial^2 E(\lambda)}{\partial \lambda^2}\bigg|_{\lambda=0} = \frac{E(\lambda_0)+E(-\lambda_0)-2E(0)}{\lambda_0^2}$$

with similar approximation for the derivatives of the dipole moment $\mu(\lambda)$. Thus, λ_0 has to be sufficiently small to maintain a linear regime. We considered the procedure satisfactory if

$$\frac{\partial \mu}{\partial \lambda}\bigg|_{\lambda=0} = \frac{\partial^2 E}{\partial \lambda^2}\bigg|_{\lambda=0} \quad .$$

For systems with a permanent dipole moment (none in this paper) a useful test is

$$\frac{\partial E}{\partial \lambda}\bigg|_{\lambda=0} = \mu(0) \quad .$$

The field strength λ_0 varied from 0.0001 a.u. to 0.003 a.u. The value $\lambda_0 = 0.003$ a.u. was appropriate for most systems but in the case of Li⁻

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the smaller value of 0.0001 a.u. was the more appropriate (see below).

4. RESULTS AND DISCUSSION .

There is a great number of studies on the polarizability of the Li and Be atoms and these systems were first selected for our test calculations. In tables 1 and 2 we summarize the experimental and theoretical results. We have no intention to cover all the literatureresults for these polarizabilities, but those results shown in the tables are representative of the best determinations available. We first mention the results of Sims *et al*.[33,37]. These have also provided rigorous lower bounds to the polarizabilities of both Li and Be. Therefore, in pre-

Table 1 - Summary of results for the dipole polarizability of the Li atom in its ^2S ground sfate. All values in $(Å)^3$. Conversion factor is I a.u. = 0.14817 $(Å)^3$.

Method	Ref.	a
Experimental		
Stark effect	5	27
Oscillator strength	6,19,20	24.4 ± 2.4
Atomic beam	21,23	22 ± 2
E-H gradient balance	24	24.3
Theoretical		
Present results	-	24.7
Configuration interaction	25	24.3
Perturbation procedure	26	24.96
Perturbation-variation	27	23.97
Sternheirner perturbation	28,29	24.74
Many-Body perturbation theory	30	24.84
Coulomb approach	31	24.3
Coupled Hartree-Fock	32	25.37
Hylleraas variation	33	24.27
Lower-bound	33	23.47

Table 2 - Summary of results for the dipole polarizability of the Be atom in its ^1S ground state. All values in $(Å)^3$. Conversion factor is 1 a.u. = $0.14817(Å)^3$.

Method	Ref.	a
Experimental		
Oscillator strength	6	$5.36 < \alpha < 6.62$
Theoretical		
Present results	-	6.6
Many-Body perturbation theory	30,34	6.93
Perturbation-variation	35	5.49
Unrestricted HF	36	6.24
Multiconfiguration SCF	32	5.41
Coupled HF	38	6.99
Uncoupled HF	23	9.54
Many-electron approach	39	5.49
Hylleraas variation	37	5.42
CI	48	5.57
PNO-CEPA	40	5.61
Coupled HF	58	6.76
MCTDHF	59	5.58
Lower bound	37	5.297

paring tables 1 and 2 all previous values not obeying these bounds were discarded. For the results reported in tables 1 and 2 the Hylleraas variation-procedure calculations of refs. 33 and 37 are among the best ones. This gives good agreement with the highly correlated calculation of Werner and Meyer[40] and, for Be, also the results of Grahan and Yeager[59]. The approach of Sims et al[33,37] includes a very accurate Hylleraas - Configuration-Interaction (CI) calculation of the wave function and therefrom the polarizability is obtained. The resulting values of $24.27(Å)^3$ for Li and $5.42(Å)^3$ for Be are believed[33,37] to be accurate

to within 2-5%. For neutral Li core-core and core-valence correlations do not significantly affect the polarizability[25] and this explains the very good agreement of our results; as for Be the result should be considered as less accurate. The very recent results of Grahan and Yeager[59] for the polarizability of Be using the MCTDHF approach are probably the best results available ($\alpha = 5.58 \overset{O}{A}^3$).

　　　　We now report on the results for Li⁻. This anion is highly polarizable with the two valence electrons occupying a very diffuse orbital. Therefore, the external electric field λ_0 has to be considerably small to maintain the regime of the finite field approach; additionally, more diffuse functions have to be included, The inclusion of correlation effects is not wise before these two points are met. For the first, we find that $\lambda_0 = 0.0001$ a.u. is appropriate for the polarizability, as discussed in the previous section. Regarding the second point, several calculations were performed. We started from the basis $(10s5p|5s3p)$ previously described and added more and more uncontracted diffuse functions by extrapolation of the exponents, following Raffenetti's recipe[41], until the polarizability value was stabilized. In table 3 we show this behavior. The results stabilize at a = 1201 a.u. and the largest basis includes an extensive set of diffuse s and p functions. The last exponents are as small as $\xi(s) = 0.00003$ and $\xi(p) = 0.0003$ and the final result for the polarizability should be considered as essentially free from basis set defficiency. For comparison Pouchan and Bishop[25] have found values changing from 870 a.u. to 1310 a.u., but their results have a poor convergence with respect to the increase of diffuse functions in the basis set. It has been found[10] indeed, that the use of unsaturated basis sets may yield α values higher than the HF limit, Our result of

Table 3 - Present calculation of the dipole polarizability of Li⁻ in its ^1S ground state as a function of basis set size (see text for notation). To enhance the variation of the polarizability, values are given in atomic units.

Basis set	$<10s5p|5s3p>$	$<11s6p|6s4p>$	$<12s6p|7s4p>$	$<13s7p|8s5p>$	$<14s7p|9s5p>$	$<15s8p|10s6p>$
α (a.u.)	·875	1183	1199	1201	1201	1201

a = 1201 a.u is the best SCF determination of the dipole polarizability of Li⁻ now available.

The compilation of results for Li⁻ is given in table 4. There has been considerable disagreement among different theoretical calculations and experimental data are not available. The first theoretical attempt to obtain this polarizability seems to be the Kirkwood-Pople-Schofield calculation by Thornallsson et al.[42]. They found a value of $269(Å)^3$. We believe that this value is of low accuracy. This conclusion is reached by comparing their results for neutral Li, which give the value of $16(Å)^3$, to the results of table 1. This value is actually well below the accurate lower bound of Sims et al.[33]. Chronologically, the next estimate was given by Tiwari et al.[29] who applied the Sternheimer method and obtained a = $283(Å)^3$. Correlated calculations were performed by Moorest and Norcross[43] and Lamm et al.[44] and they found considerably lower values of a around $120(Å)^3$. In a recent investigation Pouchan and Bishop[25] calculated a from both correlated and uncorrelated wavefunctions. They found that correlation has a dramatic effect and pratically halves the SCF value to a final result of $96(Å)^3$.

Table 4 - Summary of' results for the dipole polarizabilities of Li⁻ in its ^1S ground state. All results are theoretical value and given in $(Å)^3$. Conversion factor is 1 a.u. = $0.14817(Å)^3$.

Method	Ref.	a
Present results	-	178
Kirkwood-Pople-Schofield technique	42	269
Sternheimer	29	283
SCF	25	193
CI - dipole-velocity	43	118
CI - dipole-length	43	123
CI - pseudo-potential	44	120
CI	25	96

Li_2 is the simplest of the small alkali-metal clusters and has been of much theoretical and experimental interest[45-51]. In particular, the determination of its polarizability has been the focus of some attention[48-51]. Therefore, we have selected Li_2 and Li_2^+ for our test calculations on simple molecules,

In table 5 we compare our results with those previously obtained. This includes the SCF results of Dixon *et al.*[49], the CI calculation of Gready *et al.*[48] and the pseudo potential treatment of Bishop and Pouchan[50]. For Li_2 there is considerable agreement among all uncorrelated calculations and the results are in fairly good agreement with experiment. The best result compared to experiment is the thermodynamically averaged CI result of ref, 50. For Li_2^+ the sole result to compare with is the one of ref. 50. In this case we find perfect agreement for both components of the polarizability, which is seen to be essentially isotropic. The correlation contribution to this dipole polarizability seems thus to be fairly small and apparentiy a SCF calculation with a reasonably flexible basis set should be able to give good results. Unfortunately., there are no further results available to confirm this assertion,

5. CONCLUSIONS AND PERSPECTIVES

The best way to asses the accuracy cf these calculations if of course by direct comparison with reliable experimental data. However, in the sake of our theoretical studies it becomes particularly important to discuss the sources of inaccuracies. In this direction three major points should be raised, First, the HF calculations areperformedwithin the algebraic approximation in which the one particle states are expanded into some finite basis set, For the calculation of polarizabilities these basis sets should be flexible enough to allow the distortion of the electronic distribution provoked by the electricfield. In the calculations presented here the systems are small enough to facilitate the use of extended basis sets. We believe that both the energy and the polarizability are well given by these basis sets, The case of Li^- is exceptional and a very extended set of diffuse functions was required. Second, in adopting the non-perturbative approach and calcu-

Table 5 - Summary of the dipole polarizabilities of Li, and Li,$^+$ Both the parallel and perpendicular components are shown. All values in $(\mathring{A})^3$. The internuclear distances are 5.26 α_0 and 5.97 α_0 for Li$_2$ and Li$_2^+$, respectively, except where indicated.

	Method	Ref. .	$\alpha_{\shortparallel}$	$\alpha_{\perp}$	$\alpha_0^{(a)}$
Li$_2$:	Present results	-	40.6	27.4	31.8
	SCF	49	40,1	27.2	31.5
	SCF pseudo potential	50	40.7	25.2	30.4
	CI (R = 5.051α_0)	48	46.8	25.1	32.4
	CI pseudo potential(b)	50	55.6	21.3	32.7
	Experimental $^{(c)}$	51	-	-	33.9±3
Li$_2^+$:	Present results	-	9.3	8.4	8.7
	CI pseudo potential $^{(b)}$	50	9.3	8.4	8.7

(a) α_0 = (a,, + 2$\alpha_\perp$)/3; (b) Thermodynamically averaged values; (c) Experimental result at T = 990K.

lating the polarizability from finite differentiation of field-dependent energy and dipole moment, the proper selection of the field strength is of importance. Most systems required a value of λ_0 typically of 0.003 a.u. The case of Li$^-$ is again special in the sense that, having a high polarizability, the finite differentiation procedure required a considerably smaller value of λ_c to avoid drastic changes in the electronic distribution. Finally, as all calculations were performed within the confines of the HF approach the correlation contributions are entirely missing.

If the three points above are not met any good agreement should be considered as a fortuitous error cancellation. Obviously, this fortunate error cancellation should not be expected in the general case. On the other hand, if the two first points discussed above are carefully

considered the essential error is isolated as the correlation error. In this paper this has been the main concern. If these two points are first solved then correlation is the next important step. It is our intention to proceed to the calculation of polarizabilities by solving these two points as in this paper, and further introduce correlation corrections via a many-body perturbation theory (MBPT)[52-55] within the finite-field approach. In this case the only legitimate way of calculating the polarizability is by taking the second derivative of the energy. The derivative of the dipole moment is no longer a justified procedure[55]. In MBPT the first correlation correction is given by the second-order energy, which in the Møller-Plesset[56] scheme requires only one diagram. The next correction requires three more diagrams and leads to the generally accurate third-order results[57]. The next step is the *state-of-the-art* complete fourth-order which requires 39 additional diagrams with singly, doubly, triply and quadruply excited intermediates with respect to the reference SCF wavefunction[52]. Results at this level of calculation[53-54] are by all present standards of good accuracy. However, for both Be[60] and Li[-61] near-degeneracies severely affect the convergence of the MBPT series.

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Resumo

A experiência de se calcular polarizabilidades atômica e molecular na aproximaçao de Hartree-Fock utilizando o esquema de campo finito é descrita. Sistemas simples(Li, Li$^-$, Li$_2$, Li$_2^+$, 8e) são selecionados para facilitar o uso de funçoes base extensas. Para Li$^-$ um conjunto bastante extenso de funçoes base, incluindo um grande número de funções difusas e de polarização é necessário para se atingir um valor estável. Os resultados são comparados com outros dados experimentais e teóricos e possivelmente estão nos limites de precisão do modelo de Hartree-Fock, O erro restante é então isolado como essencialmente o erro de correlação. A inclusão de correções de correlação é discutida e adiada para um estágio posterior.