Frequency-dependent polarizabilities and Verdet constants for He, Be, CO, and FH

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Frequency dependent polarizabilities and Verdet constants for He, Be, CO, and FH have been calculated within a first (coupled Hartree–Fock) and second order polarization propagator approach. Except for regions close to excitation thresholds, small differences are found between frequency-dependent polarizabilities calculated in the two orders. The improvements in the polarizability near an excitation threshold are caused by the better description of the excitation spectrum in the second order theory. The trends in the Verdet constants are similar to those found for the polarizability except that the improvements in the second order approach are substantial also away from an excitation threshold (up to 60% of the difference between the coupled Hartree–Fock and the experimental result).

I. INTRODUCTION

Numerical calculations of second order optical properties are often based on an expansion of the wavefunctions for the ground and excited states in a finite basis set. In principle, second order properties require an infinite summation (integration) over all excited states, and very large and flexible basis sets must therefore be used to obtain reliable results. For the He atom a large basis set of the Hylleraas type has been used to compute the frequency dependent polarizability, including upper and lower bounds.[1] The polarizability in the frequency region below the first excitation threshold has been determined very accurately, whereas the bounds on the polarizability in the frequency region beyond the first excitation threshold are much wider. For larger systems less accurate calculations are available. The complexity of these systems makes it impossible to use basis sets of the same quality as for He. The basis functions of the Slater or Gaussian type which are normally used do not give a satisfactory representation of the continuum either. Some authors eliminate the basis set problem by using basis sets which are optimized to describe the second order properties[2] and obtain very accurate polarizabilities in this fashion.[3-5] These optimized basis sets do, however, often describe other second order properties and related quantities as, e.g., individual excitation energies very poorly, and are thus of limited value only.

In this communication we calculate the frequency-dependent polarizability, the Verdet constants, and energy weighted sum rules for He, Be, CO, and FH using the procedure described in the previous publication.[6] The calculations are based on the first and second order polarization propagator approach.[7] This approach has the advantage of not requiring explicit knowledge of individual excited states.[6] The first order polarization propagator approach is identical to the random phase, the time dependent Hartree–Fock and the coupled Hartree–Fock approach. The description of the frequency dependent properties is considerably better in the second order than in the first order approach and the improvement is especially noticeable in regions close to excitation thresholds, mainly due to a better description of the excitation spectrum in the second order approach. We will demonstrate this latter point by evaluating the lowest excitation energies in the two methods.

In the next section the analysis of the polarizability for He, Be, CO, and FH will be performed and the He result compared with the accurate result of Glover and Weinhold.[1] Values for the Verdet constant and the energy weighted sum rules will also be reported in Sec. II. In Sec. III we discuss the obtained result and present some concluding remarks.

II. RESULTS

A. He

We have used the basis set in Table I consisting of 48 Slater type orbitals (STO's) to calculate the frequency

TABLE I. The basis set for He (Slater type orbitals).

Type	Exponents
1s	1.45286
	2.77954
	4.34600
2s	2.0
	1.2
3s	2.0
	0.9
4s	0.8
	0.6
5s	0.6
2p	3.0
	1.9
	1.2
3p	2.0
	0.9
4p	0.8
	0.6
3d	1.5
4d	0.6
4f	0.25

TABLE II. Frequency dependent polarizabilities for the ground state of He, in atomic units.

Frequency (Hartree)	Rigorous[a] bounds	TDHF[b] Length	SOPPA[c] Length	Mixed	Velocity[d]	Velocity[e]
0.000	1.38335 ± 0.00076	1.322	1.328	1.330		1.336
0.050	1.38722 ± 0.00077	1.325	1.332	1.334		1.343
0.100	1.39898 ± 0.00078	1.336	1.343	1.345		1.365
0.150	1.41912 ± 0.00080	1.354	1.361	1.364	− 0.037	1.403
0.200	1.44851 ± 0.00083	1.380	1.389	1.391	0.606	1.461
0.250	1.48853 ± 0.00087	1.416	1.426	1.428	0.928	1.542
0.300	1.54119 ± 0.00093	1.462	1.475	1.477	1.132	1.652
0.350	1.60956 ± 0.00100	1.522	1.538	1.541	1.289	1.802
0.400	1.6983 ± 0.0011	1.600	1.620	1.623	1.433	
0.450	1.8145 ± 0.0013	1.701	1.727	1.731	1.582	
0.500	1.9705 ± 0.0015	1.834	1.870	1.875	1.758	
0.550	2.1875 ± 0.0018	2.015	2.068	2.075	1.980	
0.600	2.5091 ± 0.0023	2.275	2.359	2.368	2.293	
0.650	3.0391 ± 0.0034	2.683	2.834	2.847	2.789	
0.700	4.1184 ± 0.0073	3.434	3.782	3.805	3.766	
0.750	8.1640 ± 0.0761	5.486	7.177	7.235	7.241	
0.760		6.484	9.550	9.634	9.668	
0.770		8.169	15.751	15.905	16.011	
0.780	− 1073.68 ± 426.47	11.728	86.024	86.977	87.893	
0.785	− 31.46 ± 0.63	15.652	− 48.245	− 48.822	− 49.452	
0.790	− 14.56 ± 0.21	25.032	− 16.704	− 16.922	− 17.189	
0.795	− 8.71 ± 0.11	79.197	− 9.138	− 9.270	− 9.449	
0.800	− 5.66 ± 0.09	− 51.740	− 5.665	− 5.758	− 5.898	
0.805	− 3.75 ± 0.09	− 17.262	− 3.609	− 3.679	− 3.795	
0.810	− 2.38 ± 0.10	− 9.372	− 2.190	− 2.245	− 2.345	
0.815	− 1.30 ± 0.12	− 5.802	− 1.089	− 1.132	− 1.220	
0.820	− 0.37 ± 0.16	− 3.707	− 0.135	− 0.168	− 0.244	
0.825	0.52 ± 0.22	− 2.274	0.799	0.776	0.709	
0.830	1.47 ± 0.34	− 1.174	1.863	1.851	1.797	
0.835	2.65 ± 0.60	− 0.236	3.367	3.371	3.333	
0.840	4.52 ± 1.31	0.657	6.432	6.470	6.466	
0.845	9.75 ± 4.81	1.630	24,872	25.118	25.326	
0.850		2.901	− 11.667	− 11.838	− 12.051	
0.855		5.104	− 3.372	− 3.451	− 3.571	
0.860		12.152	− 0.555	− 0.605	− 0.695	
0.865		− 32.230	2.618	2.598	2.539	
0.870		− 5.319	− 49.503	− 50.050	− 50.640	
0.875		− 1.595	− 2.392	− 2.476	− 2.598	
0.880		0.894	6.418	6.332	6.208	

[a]Glover and Weinhold, Ref. 1.
[b]Time-dependent Hartree−Fock (first order propagator approach).
[c]The second order polarization propagator approach.
[d]Calculated from Eq. (4) in the previous publication.[6]
[e]Calculated from Eq. (5) in the previous publication.[6]

dependent polarizabilities in Table II. The basis set consists of the Clementi−Roetti[7] STO basis for He, augmented with diffuse orbitals which describe the excited states of the atom. The exponents for the diffuse functions are chosen to minimize the difference between the dipole length and the dipole velocity oscillator strengths in the time-dependent Hartree−Fock approximation. The polarizabilities are given in the dipole length, dipole velocity, and the mixed representation. TDHF refer to the time-dependent Hartree−Fock approximation or first order polarization propagator approach.[8] The first and second order (SOPPA) polarization propagator methods are described in the preceding article.[6]

The TDHF results are to three decimal places identical to the RPA results[9] and are probably very close to

the RPA limit since the oscillator strengths in the dipole length, the mixed, and the dipole velocity formulations agree to three decimal places. Harris[10] and Jørgensen and Linderberg[11] have shown that the length, mixed, and velocity formulations are equivalent in TDHF, provided a complete basis set is used. The large discrepancy between the TDHF polarizabilities calculated by Epstein[12] in the length and velocity formulations is thus caused by the use of a very limited basis set.

The second order (SOPPA) polarizabilities change only slightly relative to the coupled HF results below the first excitation threshold (see Fig. 1) but are considerably improved close to and above the first excitation threshold (see Fig. 2). This behavior can be understood from an analysis of the individual excitation energies
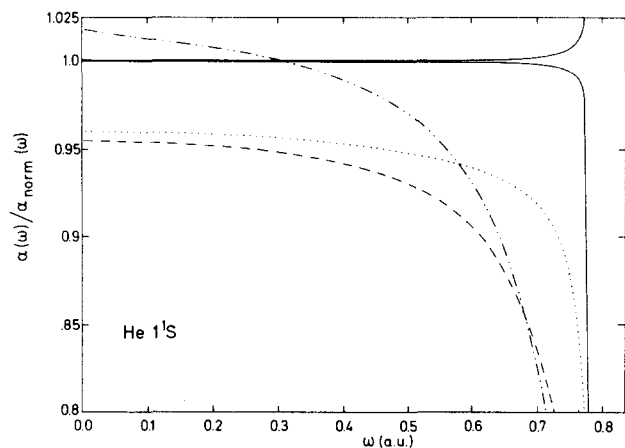
FIG. 1. Dynamic polarizability of the He (^1S) ground state for ω less than 0.78 a.u., expressed relative to the mean upper and lower bounds from Glover and Weinhold.[1] The rigorous upper and lower bounds are marked with solid lines and they are compared with our coupled HF results [identical to the RPA results[9]] (----), with the second order polarization propagator results (....) and with the many-body perturbation theory results of N. C. Dutta, T. Ishihara, C. Matsubara, and T. P. Das, Phys. Rev. Lett. 22, 8 (1969) (— ·· — ·· —).

and transition moments. We have in Table III collected information about both the dipole forbidden and the dipole allowed transitions calculated in TDHF and SOPPA. The SOPPA spectrum differs by less than 0.1 eV from the experimental[13] excitation energies and *all* the transitions are improved considerably in SOPPA compared to TDHF. In view of the substantial improvements in the excitation spectrum in SOPPA, it is somewhat surprising that the difference between the static polarizability in TDHF and

TABLE III. Excitation energies from the He ground state (in eV).

Excited state	TDHF	SOPPA	Experiment[a]
$2s(^1S)$	21.10	20.61	20.61
$2p(^1P)$	21.69	21.28	21.22
$3s(^1S)$	23.33	22.88	22.92
$3d(^1D)$	23.93	23.45	23.07
$3p(^1P)$	23.50	23.04	23.09
$4s(^1S)$	24.07	23.60	23.67
$4f(^1F)$	24.13	23.66	23.74
$4p(^1P)$	24.14	23.66	23.74
$5s(^1S)$	24.41	23.93	24.01
$5p(^1P)$	24.46	23.98	24.04
$6s(^1S)$	25.31	24.88	24.19
$2s(^3S)$	19.69	19.79	19.82
$2p(^3P)$	21.22	20.98	20.96
$3s(^3S)$	23.02	22.65	22.72
$3p(^3P)$	23.36	22.97	23.01
$3d(^3D)$	23.93	23.45	23.07
$4s(^3S)$	23.96	23.51	23.59
$4p(^3P)$	24.09	23.63	23.71
$4f(^3F)$	24.13	23.66	23.74
$5s(^3S)$	24.35	23.88	23.97
$5p(^3P)$	24.44	23.96	24.03
$6s(^3S)$	24.94	24.55	24.17

[a]C. E. Moore, Ref. 13.

TABLE IV. Contribution to the He polarizability from the bound excited states (atomic units).

	TDHF		SOPPA	
	Length	Velocity	Length	Velocity
$2p(^1P)$	0.399	0.400	0.404	0.414
$3p(^1P)$	0.099	0.100	0.099	0.100
$4p(^1P)$	0.041	0.041	0.041	0.041
$5p(^1P)$	0.020	0.020	0.022	0.022
total	0.559	0.561	0.566	0.577

SOPPA is relatively small. In Table IV we report the contribution to the static polarizability originating from the transitions $1s^2 \rightarrow 1s2p - 5p$ which are the only dipole allowed transitions that can be determined accurately in the present (limited) basis set. It appears from Table IV that the contributions to the static polarizability increase with 2%–3% from TDHF to SOPPA, whereas the polarizability itself only changes with about 1%. The extra bound state contributions to the polarizability in SOPPA is thus cancelled by a corresponding decrease in the continuum contributions making the total improvements in SOPPA small.

In Table V the transition moments calculated in the dipole length and in the dipole velocity approximation are reported.

The transition moments for the lowest transitions are about 3%–10% too low in SOPPA, and is basically unchanged compared with the TDHF value. This is probably the main reason for the remaining error of about 4% in the static polarizability. The poles are however accurately located in SOPPA, which has the effect that the frequency dependent polarizability close to and beyond the first excitation threshold is in very good agreement with the result of Glover and Weinhold.[1] We have in Fig. 2 plotted the frequency-dependent polarizability near the lowest excitation thresholds. Also the upper and lower bounds for the polarizability obtained by
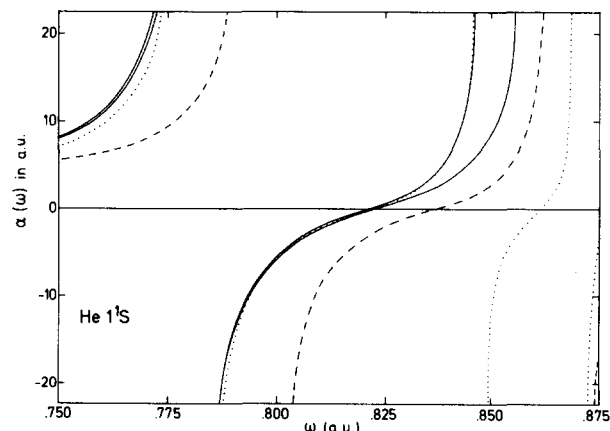

FIG. 2. Dynamic polarizability of the He (^1S) ground state for $\omega > 0.75$ a.u. The rigorous upper and lower bounds of Glover and Weinhold are marked with solid lines and the coupled HF and the second order polarization propagator results (SOPPA) have the same signature as in Fig. 1.

TABLE V. Oscillator strengths and in parentheses the squares of the corresponding transition moments (in atomic units) for the lowest dipole allowed transition in He.

Transition	Schiff *et al.*[a]		TDHF		SOPPA	
	Length	Velocity	Length	Velocity	Length	Velocity
$2p(^1P)$	0.276	0.276	0.254	0.254	0.247	0.253
	(0.531)	(0.323)	(0.477)	(0.304)	(0.474)	(0.297)
$3p(^1P)$	0.073	0.073	0.074	0.074	0.071	0.072
	(0.129)	(0.093)	(0.129)	(0.096)	(0.125)	(0.092)
$4p(^1P)$	0.030	0.030	0.033	0.033	0.031	0.031
	(0.052)	(0.039)	(0.055)	(0.043)	(0.053)	(0.041)
$5p(^1P)$	0.015	0.015	0.017	0.016	0.017	0.017
	(0.025)	(0.020)	(0.028)	(0.022)	(0.029)	(0.022)

[a]B. Schiff, C. L. Pekeris, and Y. Accad, Phys. Rev. A 4, 885 (1971).

Glover and Weinhold[1] are indicated in Fig. 2. The polarizability is clearly improved in SOPPA compared with the TDHF result. Glover and Weinhold[1] have made an extensive comparison of their result with previous calculations, and it is clear from their analysis that the SOPPA result reported here represents one of the most accurate descriptions of the frequency-dependent polarizabilities in the frequency regions above the first excitation threshold.

Table II also contains the mixed and the velocity forms for the frequency-dependent polarizability. They closely resemble the result obtained in the dipole length form. The velocity values are calculated using both Eq. (4) and Eq. (5) in Paper I. Both relations are only valid in limiting cases, Eq. (4) when the term N/E^2 is not dominating and Eq. (5) when E^2/ω_{0m} is small. From Table II it is readily seen that Eq. (4) can be used for large frequencies and Eq. (5) for small frequencies.

The basis set used for He (Table I) is relatively large compared to basis sets which can be used in practice for larger systems. Our experience has been that basis sets have to be relative large to give reliable results for both static and frequency-dependent polarizabilities. The method advocated by some authors to optimize smaller basis sets particularly for the description of static second order properties[2,5] may lead to unreliable results for the dynamic polarizability. As an illustration of this point, we have used the 12 STO basis set of Fortune and Certain[5] to calculate the static polarizabilities in the TDHF approximation and obtain 1.387 and 1.317 in the length and velocity form, respectively. Fortune and Certain list a value of 1.641 for the $2s'$ STO orbital exponent which is the value used to obtain the above polarizabilities. However, changing the exponent $\xi_{2s'}$ from 1.641 to 2.63 gives 1.322 and 1.325 in the length and in the velocity form, respectively, which are the results quoted by Fortune and Certain[5] and the value 1.641 for $\xi_{2s'}$ is probably a misprint. The experimental static polarizability is 1.383 and can thus be well reproduced by the basis of Fortune and Certain in TDHF in the length approximation. The inconsistency of the 1.387 result becomes more transparent if the individual excitation energies are calculated. The lowest excitation energy is off by 2.6 eV for both the 12

STO basis sets. The higher excitation energies cannot at all be described within these basis sets. More elaborate approximations, like, e.g., SOPPA, give worse results than TDHF with the 12 STO basis set and the frequency-*dependent* polarizability is unrealistic even for moderate frequencies at all levels of approximation.

In Table VI we report Verdet constants calculated with the Bequerel formula[14,15] in the dipole length and the mixed representation.[6] The TDHF result is very close to the TDHF limit and identical Verdet constants are calculated in the three formulations. Close agreement with previous coupled HF Verdet constants of Martin *et al.*[9] and Kaveeshwar *et al.*[16] has also been obtained. The Verdet constants in the second order approach are considerably better than those calculated in TDHF. The improvements are more pronounced than for the polarizabilities, especially in regions far from excitation thresholds. Thus, up to 60% of the difference between the coupled HF and experimental result have been accounted for in SOPPA in the frequency regions where the experimental results are available.[17]

In Table VII we report the sum rules $S(0)$ and $S(-2)$ calculated within SECI, TDHF, and SOPPA using both the length, the velocity and the mixed representation. As discussed in Paper I, the mixed representation of $S(0)$ is independent of the approximation level used for the propagator.[18] The $S(0)$ sum rule is accurately fulfilled at the TDHF level of approximation indicating that the basis set is nearly complete. The formal equivalence of the length, mixed, and velocity representation in TDHF does not hold at the SOPPA level of approximation and we find a larger deviation among the various formulations in SOPPA (see Table VII). The fulfillment of the $S(0)$ sum rule in TDHF does, however, not ensure that the individual transition moments and excitation energies, which enter in $S(0)$, are accurately determined. The equivalence represents an intrinsic consistency of the TDHF approximation.[10,11,18] This consistency of TDHF makes it advantageous to use TDHF as a first order approximation for improved description of response properties.

The singly-excited configuration interaction approximation (SECI) can be considered as a first order approx-

TABLE VI. Verdet constant for He in units of μmin oersted^{-1} atm^{-1} cm^{-1}.

Wave-length (Å)	Experi-ment[a]	TDHF Length	SOPPA Length	SOPPA Mixed
517.77		1.274(+4)	1.689(+5)	1.684(+5)
520.72		1.137(+4)	2.117(+4)	2.131(+4)
523.72		2.638(+4)	3.009(+6)	3.039(+6)
526.74		5.645(+5)	2.236(+4)	2.258(+4)
529.81		6.967(+4)	1.061(+4)	1.071(+4)
532.90		1.396(+4)	1.618(+4)	1.635(+4)
536.04		6.646(+3)	8.592(+4)	8.689(+4)
539.21		4.573(+3)	3.021(+5)	3.055(+5)
542.42		3.860(+3)	2.138(+4)	2.161(+4)
545.67		3.788(+3)	8.201(+3)	8.289(+3)
548.96		4.184(+3)	5.061(+3)	5.114(+3)
552.28		5.132(+3)	4.037(+3)	4.079(+3)
555.65		6.995(+4)	3.829(+3)	3.869(+3)
559.06		1.081(+4)	4.142(+3)	4.186(+3)
556.51		2.003(+4)	5.013(+3)	5.067(+3)
556.00		5.206(+4)	6.768(+3)	6.842(+3)
569.54		3.775(+5)	1.037(+4)	1.048(+4)
573.12		7.409(+5)	1.903(+4)	1.924(+4)
576.75		6.375(+4)	4.855(+4)	4.910(+4)
580.42		2.193(+4)	3.262(+5)	3.299(+5)
584.15		1.101(+4)	8.680(+5)	8.779(+5)
591.73		4.436(+3)	2.203(+4)	2.228(+4)
559.52		2.404(+3)	6.565(+3)	6.639(+3)
607.51		1.516(+3)	3.138(+3)	3.172(+3)
650.91		3.830(+2)	5.133(+2)	5.184(+2)
700.97		1.728(+2)	2.065(+2)	2.083(+2)
759.39		9.634(+1)	1.093(+2)	1.102(+2)
828.42		5.590(+1)	6.558(+1)	6.607(+1)
911.27		3.087(+1)	4.204(+1)	4.233(+1)
1000.00		2.730(+1)	2.920(+1)	2.940(+1)
1139.08		1.778(+1)	1.882(+1)	1.894(+1)
1215.70		1.464(+1)	1.544(+1)	1.554(+1)
1301.81		1.206(+1)	1.268(+1)	1.276(+1)
1518.78		8.036	8.411	8.462
1822.53		5.160	5.381	5.413
2278.17		3.107	3.230	3.249
2500.00		2.533	2.632	2.648
3037.56		1.669	1.732	1.742
3635.00	1.25	1.145	1.187	1.194
4000.00	1.01	9.390(−1)	9.735(−1)	9.791(−1)
4500.00	8.00(−1)	7.368(−1)	7.637(−1)	7.680(−1)
5000.00	6.38(−1)	5.939(−1)	6.154(−1)	6.189(−1)
5460.00	5.31(−1)	4.963(−1)	5.142(−1)	5.172(−1)
5500.00	5.22(−1)	4.890(−1)	5.067(−1)	5.096(−1)
5780.00	4.74(−1)	4.421(−1)	4.580(−1)	4.606(−1)
6000.00	4.41(−1)	4.098(−1)	4.245(−1)	4.269(−1)
6500.00	3.76(−1)	3.484(−1)	3.609(−1)	3.630(−1)
7000.00	3.25(−1)	2.999(−1)	3.106(−1)	3.124(−1)
7500.00	2.83(−1)	2.609(−1)	2.702(−1)	2.717(−1)
8000.00	2.46(−1)	2.290(−1)	2.372(−1)	2.386(−1)
8500.00	2.21(−1)	2.027(−1)	2.099(−1)	2.111(−1)
9000.00	2.03(−1)	1.807(−1)	1.871(−1)	1.882(−1)

[a]L. R. Ingersoll and D. H. Liebenberg, Ref. 17.

TABLE VIII. Frequency dependent polarizabilities for the ground state of Be (atomic units).

Wave-length (Å)	SOPPA Length	SOPPA Mixed	TDHF Length	TDHF Velocity
∞	43.54	40.69	45.88	45.82
10000	46.30	43.27	49.11	49.02
6000	52.20	48.80	56.14	56.02
5000	57.23	53.51	62.31	62.14
4000	69.60	65.15	78.17	77.89
3500	85.55	73.07	99.91	99.47
3000	132.46	114.80	175.77	174.73
1800	191.47	166.78	306.40	304.28
2600	431.01	377.14	···	·· ·
2400	−730.54	−641.78	−277.29	−274.39
2200	−162.24	−142.99	−116.11	−114.46
2000	−79.55	−70.23	−65.11	−63.64
1900	−60.15	−53.08	−50.65	−48.95
1800	−46.62	−41.03	−39.00	−36.07
1700	−36.67	−31.70	−36.81	−40.66
1600	−29.07	−26.60	−27.43	−27.88
1500	−23.06	−20.64	−21.84	−21.80

imation for more elaborate configuration interaction approaches. $S(0)$ is fulfilled very badly in SECI and no formal equivalence is present between the length and the velocity formulations (see Table VII).

B. Be

We have used the 50 STO basis of Moser et al.[19] to calculate the frequency dependent polarizabilities reported in Table VIII displayed in Fig. 3. The SECI frequency dependent polarizabilities calculated within the dipole length and dipole velocity approximation differ substantially and are both far from the results obtained in TDHF and SOPPA. No experimental results are presently available. The dipole length, the mixed, and the dipole velocity forms for the frequency dependent polarizability differ very little in TDHF and only the length and velocity result are given. The larger difference between length and velocity results found in TDHF by Esptein[12] is caused by the very small basis set used in his calculations. The trends in the changes from TDHF to SOPPA are similar to those found for He, i.e., larger differences between the three formulations and a substantial change in the polarizability near the excitation threshold. None of the approximate formulas for direct evaluation of the frequency dependent polarizability in the velocity formulation [i.e., Eqs. (4) and (5) in Paper I] are valid for Be for which the lowest excitation energy is rather small and we have not reported SOPPA polarizabilities in the velocity form in Table VIII.

TABLE VII. Energy weighted sum rules, $S(n) = \sum_{k \neq 0} f_{ck} \omega_{0k}^n$, for He (atomic units).

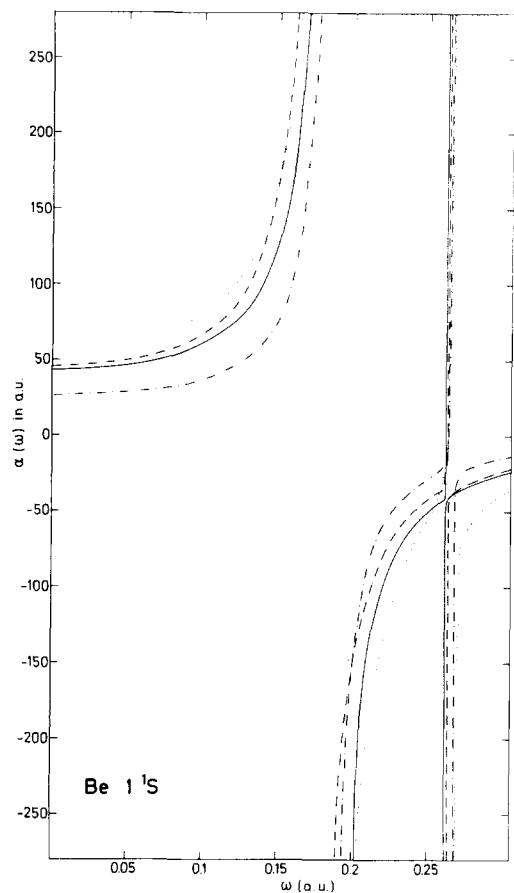| Sum rule	SECI Length	SECI Velocity	TDHF Length	TDHF Velocity	SOPPA Length	SOPPA Mixed	SOPPA Velocity
$S(0)$	2.19	1.84	2.02	2.00	2.08	2.01	2.04
$S(-2)$	1.40	1.21	1.32	1.32	1.33	1.33	1.34

FIG. 3. Dynamic polarizability of the Be(^1S) ground state in the single-excited CI approximation using the length formulation (. . . . .) and the velocity formulation (– • – • – • – • –). The first (– – – – –) and second order (————) polarization propagator results are also indicated.

We see from Table VIII that inclusion of second order correlation decreases the value of the static polarizability in agreement with previous calculations.[20–22] The SOPPA result in the dipole velocity form is 38.27. The

TABLE IX. Verdet constants for Be in units of μmin oersted^{-1} atm^{-1} cm^{-1}.

Wave-length (Å)	SOPPA		TDHF	
	Length	Mixed	Length	Velocity
10000	1.484(+2)	1.390(+2)	5.820(+1)	5.790(+1)
6000	5.266(+2)	4.933(+2)	2.124(+2)	2.111(+2)
5000	9.147(+2)	8.569(+2)	3.779(+2)	3.753(+2)
4000	2.131(+3)	1.996(+3)	9.345(+2)	9.278(+2)
3500	3.812(+3)	3.956(+3)	2.004(+3)	1.989(+3)
3000	1.229(+4)	1.303(+4)	8.516(+3)	8.446(+3)
2800	2.951(+4)	3.143(+4)	2.986(+4)	2.961(+4)
2600	1.744(+5)	1.861(+5)	6.517(+6)	6.462(+6)
2400	5.935(+5)	6.335(+5)	3.386(+4)	3.359(+4)
2200	3.535(+5)	3.768(+5)	7.185(+3)	7.139(+3)
2000	1.053(+4)	1.117(+4)	2.835(+3)	2.848(+3)
1900	6.790(+3)	7.177(+3)	2.006(+3)	2.077(+3)
1800	4.696(+3)	4.887(+3)	1.816(+3)	2.301(+3)
1700	3.939(+3)	3.433(+3)	2.764(+3)	4.759(+3)
1600	3.161(+3)	2.501(+3)	8.700(+2)	9.823(+2)
1500	1.906(+3)	1.919(+3)	6.239(+2)	6.610(+2)

TABLE X. Basis set for carbon monoxide (Slater type orbitals).

Type	Center	Exponents
1s	C	5.67263
2s	C	1.15282
		1.83062
3s	C	0.8
4s	C	0.2
2p	C	2.73045
		1.25656
3p	C	0.8
3d	C	0.8
3$d_{\pm2}$	C	0.25
4$d_{\pm2}$	C	0.2
1s	O	7.6579
2s	O	1.67543
		2.68801
3s	O	0.5
4s	O	0.2
2p	O	1.65864
		3.69445
3p	O	0.5
3d	O	0.5
3$d_{\pm2}$	O	0.2
4$d_{\pm2}$	O	0.2

TABLE XI. Polarizabilities[a] for the ground state of CO, parallel to the internuclear axis (atomic units).

Wave-length (Å)	TDHF		SOPPA	
	Length	Velocity	Length	Mixed
∞	12.75	9.39	12.75	11.69
20000	12.77	9.40	12.77	11.71
10000	12.82	9.44	12.83	11.77
8000	12.85	9.47	12.88	11.82
6328	12.91	9.51	12.96 (15.73[b])	11.90
5790	12.95	9.55	13.00	11.94
4800	13.05	9.63	13.11	12.05
2894	13.63	10.11	13.80	12.75
2676	13.79	10.24	14.00	12.95
2211.6	14.35	10.71	14.70	13.66
1850.7	15.22	11.44	15.81	14.78
1742.7	15.63	11.78	16.35	15.34
1672	15.97	12.07	16.81	15.80
1600	16.38	12.41	17.37	16.38
1500	17.12	13.04	18.43	17.46
1440	17.70	13.54	19.28	18.34
1410	18.04	13.83	19.80	18.87
1380	18.42	14.16	20.40	19.49
1350	18.86	14.53	21.10	20.22
1300	19.73	15.28	22.59	21.76
1200	22.38	17.60	28.15	27.57
1160	24.07	19.09	33.60	33.24
1140	25.17	20.07	40.01	39.79
1120	26.52	21.27	93.92	93.00
1100	28.25	22.82	28.05	29.36
1080	30.60	24.92	47.56	50.49
1060	34.12	28.07	129.38	144.73
1040	40.61	33.82	−23.98	−33.78
1020	62.97	53.10	11.60	6.83
1000	−12.62	−9.55	25.02	21.59

[a]At the internuclear separation $R = 2.132$ bohr.
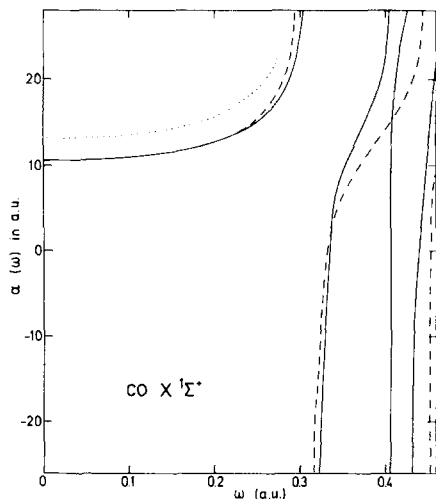[b]Experimental value from Ref. 25.

FIG. 4. The isotropic component of the frequency-dependent polarizability for the ground state of CO in the time-dependent Hartree—Fock (dashed curve) and the second order polarization propagator approximation (solid curve) both calculated in the dipole length approximation. The dotted curves are the experimental values from Ref. 24.

Be atom shows the peculiarity that more than 95% of the contribution to the static polarizability originates from the lowest dipole allowed transition. We have previously[23] analyzed this transition together with other dipole

TABLE XII. Polarizabilities[a] for the ground state of CO, perpendicular to the internuclear axis (atomic units).

Wave- length (Å)	TDHF		SOPPA	
	Length	Velocity	Length	Mixed
∞	9.43	9.14	9.55	9.08
20000	9.45	9.16	9.57	9.11
10000	9.53	9.24	9.64	9.17
8000	9.58	9.29	9.69	9.22
6328	9.67	9.38	9.77	9.30
			(12.14[b])	
5790	9.72	9.43	9.82	9.35
4800	9.86	9.57	9.96	9.48
2894	10.79	10.52	10.83	10.30
2676	11.09	10.82	11.11	10.56
2211.6	12.29	12.05	12.17	11.55
1850.7	15.01	14.84	14.37	13.59
1742.7	17.05	16.94	15.86	14.97
1672	19.43	19.40	17.46	16.44
1600	24.19	24.33	20.31	19.04
1500	57.84	59.27	32.87	30.44
1440	− 85.62	− 89.83	136.83	124.35
1410	− 26.74	− 28.66	− 69.74	− 62.16
1380	− 12.15	− 13.51	− 17.83	− 15.25
1350	− 5.43	− 6.54	− 5.57	− 4.15
1300	0.38	− 0.54	2.57	3.27
1200	6.08	5.27	9.93	10.12
1160	7.73	6.91	12.53	12.61
1140	8.53	7.70	14.08	14.11
1120	9.35	8.50	16.02	16.00
1100	10.23	9.34	18.81	18.73
1080	11.19	10.25	23.97	23.76
1060	12.29	11.28	43.44	42.74
1040	13.63	12.48	− 19.98	− 18.95
1020	15.37	14.02	7.76	8.11
1000	17.95	16.21	15.31	15.54

[a]At the internuclear separation R = 2.132 bohr.
[b]Experimental value from Ref. 25.

TABLE XIII. Vertical excitation energies (in eV) from the $X^1\Sigma^+$ ground state of CO at 2.132 bohr.

STATE	TDHF	SOPPA	SOPPA +ESHIFT[a]	Exp[b]
$a\,^3\Pi$	5.15	6.34	5.90	6.4
$A\,^1\Pi$	8.49	8.68	8.70	8.5
$a'\,^3\Sigma^+$	6.14	8.84	8.22	8.6
$e\,^3\Sigma^-$	9.19	10.31	9.61	9.9
$d\,^3\Delta$	7.89	9.76	9.14	9.5
$I\,^1\Sigma^-$	9.19	10.50	10.49	10.2
$D\,^1\Delta$	9.89	10.65	10.74	~ 10.8
$B\,^1\Sigma^+$	12.30	11.09	11.26	10.9
$C\,^1\Sigma^+$	13.07	11.73	11.91	~ 11.4

[a]The second order polarization propagator approximation with energy-shifted denominators, see text and Ref. 23.
[b]The vertical excitation energies are computed from the potential curves and spectroscopic constants given by Krupenie[28] ($a\,^3\Pi$, $a'\,^3\Pi$, $d\,^3\Delta$, $A\,^1\Pi$ and $B\,^1\Sigma^+$) and by Herzberg et al.[29,30] and Simmons and Tilford[31] ($I\,^1\Sigma^-$, $e\,^3\Sigma^-$ and $D\,^1\Delta$) and Meyer et al.[32] ($C\,^1\Sigma^+$).

allowed and forbidden transitions using the same basis set[19] as in this calculation. Even though a considerable improvement was obtained for the $1s^22s2p(^1P)$ transition in SOPPA compared with TDHF, the excitation energy deviated with 3% and the transition moment with 10% from the experimental values. This discrepancy is larger than the error usually present in SOPPA and reflects the fact that the ground state is highly correlated and the transition thus difficult to describe in a finite perturbational approach. The differences between the polarizability in the various formulations are thus solely caused by the difficulties in describing the lowest dipole allowed transition. A more accurate description of this transition would probably lead to a polarizability of about 39.5 which we expect would be close to the experimental one. A detailed comparison between previous calculated static polarizabilities can be found in Ref. 22.

In Table IX we report Verdet constants calculated within the TDHF and the SOPPA approximation. No experimental results are presently available. We would expect the quality of the reported SOPPA result to be the same as for He. Particularly in the regions close to the excitation thresholds do we expect the SOPPA result to be superior to the TDHF result.

C. CO

We have used the basis set in Table X consisting of 46 STO's to calculate the frequency dependent polarizabilities in Table XI (parallel component) and Table XII (perpendicular component). The basis set consists of single zeta 1s STO's and double zeta the 2s and 2p STO's augmented with appropriate diffuse orbitals. The exponents for the 1s, 2s, and 2p orbitals were taken from the tables by Clementi and Roetti[7] and the rest of the exponents were optimized in the same way as described for Helium. The mean polarizability is plotted in Fig. 4 together with the available experimental data.[24] The anisotropy is only measured[25] at 6328 Å and the derived values for $\alpha_\parallel(\omega)$ and $\alpha_\perp(\omega)$ are given in Tables X and XI.

TABLE XIV. The isotropic component of the Verdet constant[a] for CO in units of μmin oersted^{-1} atm^{-1} cm^{-1}.

Wavelength (Å)	TDHF Length	SOPPA Length	SOPPA Mixed	Experiment[b]
1000	5.60(+4)	1.05(+4)	1.09(+4)	
1020	2.57(+4)	1.62(+4)	1.68(+4)	
1040	5.53(+3)	1.11(+5)	1.15(+5)	
1060	3.07(+3)	1.86(+5)	2.06(+5)	
1080	3.20(+3)	1.81(+4)	1.94(+4)	
1100	1.76(+3)	1.38(+4)	1.40(+4)	
1120	1.51(+3)	1.65(+5)	1.62(+5)	
1140	1.36(+3)	6.57(+3)	6.59(+3)	
1160	1.27(+3)	3.45(+3)	3.47(+3)	
1200	1.23(+3)	2.17(+3)	2.16(+3)	
1300	2.04(+3)	2.72(+3)	2.54(+3)	
1350	3.93(+3)	6.13(+3)	5.59(+3)	
1380	7.27(+3)	1.55(+4)	1.41(+4)	
1410	1.86(+4)	1.10(+5)	1.00(+5)	
1440	1.20(+5)	2.52(+5)	2.28(+5)	
1500	2.94(+4)	7.55(+3)	6.90(+3)	
1600	2.76(+3)	1.60(+3)	1.47(+3)	
1672	1.32(+3)	9.13(+2)	8.42(+2)	
1850.7	4.88(+2)	4.01(+2)	3.77(+2)	
2676	9.27(+1)	9.02(+1)	8.66(+1)	
3635	3.99(+1)	4.00(+1)	3.85(+1)	3.15(+1) [0.79]
4000	3.16(+1)	3.18(+1)	3.07(+1)	2.47(+1) [0.78]
4360	2.58(+1)	2.61(+1)	2.51(+1)	2.03(+1) [0.78]
4500	2.40(+1)	2.43(+1)	2.34(+1)	1.90(+1) [0.78]
5000	1.89(+1)	1.92(+1)	1.85(+1)	1.51(+1) [0.79]
5460	1.56(+1)	1.58(+1)	1.53(+1)	1.25(+1) [0.79]
5500	1.53(+1)	1.56(+1)	1.50(+1)	1.23(+1) [0.79]
5780	1.37(+1)	1.40(+1)	1.35(+1)	1.10(+1) [0.79]
5893	1.32(+1)	1.34(+1)	1.30(+1)	1.05(+1) [0.79]
6000	1.27(+1)	1.29(+1)	1.25(+1)	1.01(+1) [0.78]
6500	1.07(+1)	1.09(+1)	1.05(+1)	8.47 [0.78]
7000	9.13	9.30	8.99	7.21 [0.78]
7500	7.89	8.05	7.78	6.21 [0.77]
8000	6.90	7.04	6.80	5.46 [0.78]
8500	6.08	6.21	6.00	4.83 [0.79]
9000	5.40	5.52	5.33	4.30 [0.78]
9875	4.46	4.56	4.41	3.60 [0.79]
20000	1.06	1.09	1.05	

[a]At $R = 2.132$ bohr.

[b]Ingersoll and Liebenberg, Ref. 17. The number in square brackets [ ] is the ratio between the value calculated in SOPPA (length) and the experimental value.

To the authors' knowledge no other calculation of the frequency dependent polarizability has been reported in the literature whereas there exist a few calculations of the static polarizability (see Werner and Meyer[26] for a review).

The rather large difference between the TDHF polarizabilities in the length and velocity formulation, especially for $\alpha_{\shortparallel}$, is a consequence of the limited basis set. The static mean polarizability is 10.54 a.u. (length) compared with the TDHF limit result[26] of 12.40 a.u. Inclusion of second order correlation does not improve the polarizabilities much for small energies which follow the trends observed for atoms. We see, however, from Fig. 4 that the dispersion of the polarizability is well represented in the second order theory, but that there is a sizeable shift between the calculated and observed frequency dependent polarizability. For frequen-

TABLE XV. Polarizabilities[a] for the ground state of hydrogen fluoride parallel to the internuclear axis (atomic units).

Wavelength (Å)	TDHF Length	TDHF Velocity	SOPPA Length	SOPPA Mixed	SOPPA Velocity
∞	5.49	5.55	5.64	5.99	6.46
10000	5.51	5.57	5.64	5.99	
4500	5.59	5.65	5.74	6.10	
3000	5.71	5.79	5.88	6.27	
2000	6.04	6.12	6.28	6.71	
1600	6.41	6.52	6.79	7.28	
1400	6.80	6.92	7.30	7.86	
1300	7.09	7.24	7.75	8.37	
1200	7.53	7.70	8.41	9.12	
1150	7.83	8.02	8.90	9.67	
1100	8.22	8.43	9.55	10.42	
1050	8.75	8.98	10.48	11.46	
1000	9.49	9.76	12.00	13.21	
950	10.61	10.96	14.67	16.28	
900	12.61	13.07	20.62	22.79	
850	17.48	18.25	54.93	61.74	
800	−56.96	−61.24			

[a]At $R = 1.733$ bohr.

cies near and above the first excitation threshold we expect the second order polarizabilities to be substantially better than the coupled HF results due to a much better description of the excitation spectrum in SOPPA. This is illustrated in Table XIII. The tendency is the same as for He but the change from TDHF to SOPPA is considerably larger for CO. We have also computed the excitation energies in the second order polarization propagator approach with energy shifted denominators,[23] a technique which is often used in many-body perturbation theory.[27] The agreement with experiment[28–32] is, however, not improved in the shifted approximation which is in agreement with earlier findings for smaller systems.[23]

TABLE XVI. Polarizabilities[a] for the ground state of hydrogen fluoride, perpendicular to the internuclear axis (atomic units).

| Wavelength (Å)	TDHF Length	TDHF Velocity	SOPPA Length	SOPPA Mixed	SOPPA Velocity
∞	4.13	3.99	4.31	4.50	4.81
10000	4.15	4.01	4.33	4.51	
4500	4.19	4.06	4.40	4.60	
3000	4.29	4.16	4.54	4.76	
2000	4.53	4.41	4.91	5.19	
1600	4.84	4.73	5.49	5.89	
1400	5.20	5.12	6.48	7.10	
1300	5.55	5.48	8.38	9.44	
1200	6.27	6.23	−12.11	−15.91	
1150	7.05	7.05	1.75	1.21	
1100	9.18	9.26	3.88	3.84	
1050	146.30	150.46	5.15	5.41	
1000	1.32	1.21	6.66	7.29	
950	3.87	3.90	10.89	12.69	
900	5.23	5.41	−7.75	−11.51	
850	7.09	7.66	2.71	1.86	
800	22.42	27.74	5.32	4.96	

[a]At $R = 1.733$ bohr.
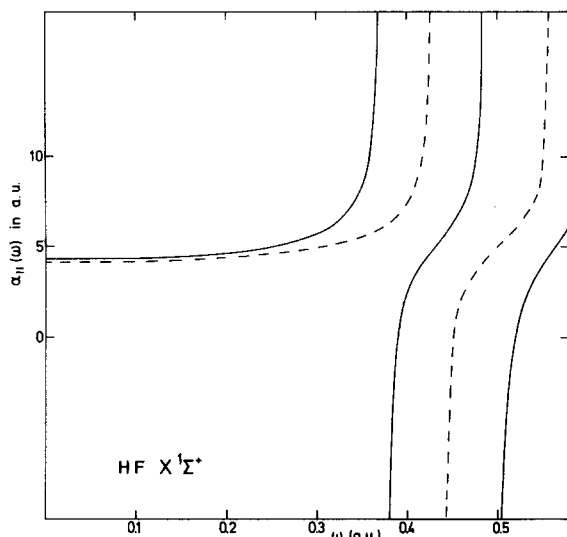
FIG. 5. The parallel component $(\alpha_\parallel)$ of frequency-dependent polarizability for the ground state of hydrogen fluoride in TDHF (dashed curve) and SOPPA (solid curve).

We have also calculated the Verdet constant for CO and the results are given in Table XIV. We have used the Becquerel[14] formula [see Eq. (50) in Paper I] which is only valid for atoms. Serber[33] showed that the Verdet constant for diatomic molecules for frequencies well away from absorption edges instead is given by

$$V(E) = r \frac{e}{2mc^2} E \frac{dn(E)}{dE} , \qquad (1)$$

where r is an empirical, frequency-independent factor which should vary between 1 (central field) and 0.5 (line field). The dispersion of the Faraday rotation should thus be given by the Becquerel formula and this is clearly fulfilled for the calculated Verdet constants in Table XIV. We find that $r(CO) = 0.78(9)$ which is in good agreement with the Serber prediction. From the calculation on He we know that SOPPA normally predicts slightly too small values for the Verdet constants, so the present value for $r(CO)$ should be considered an upper bound to the true value. For comparison we may add that Langhoff[34] from a moment calculation of the Verdet constants finds that $r(O_2) = 0.30$ and $r(N_2) = 0.64$.

D. FH

The basis set used for FH is an extension of the one used by Bender and Davidson[35] and is the 45 STO basis

TABLE XVII. Excitation energies (in eV) from the ground state of hydrogen fluoride at $R = 1.733$ bohr.

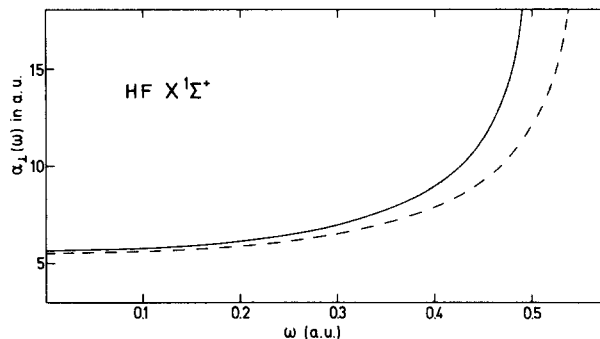|	TDHF	SOPPA	Experiment[a]	CI[b]
$^3\Pi$ (1)	10.95	9.78	⋯	10.13
$^3\Sigma^+$ (1)	14.59	13.30	⋯	13.52
$^1\Pi$ (1)	11.82	10.21	⋯	10.66
$B\,^1\Sigma^+$	15.43	13.43	13.63	

[a]Reference 37.
[b]Reference 38 at $R = 1.75$ bohr.

FIG. 6. Same as in Fig. 5 except that this is the perpendicular component, $\alpha_\perp(\omega)$.

given in Table IV of Ref. 36. The frequency dependent polarizabilities calculated in TDHF and in SOPPA are given in Tables XV and XVI and are displayed in Figs. 5 and 6 for $\alpha_\parallel$ and $\alpha_\perp$, respectively. We see a substantial change in the frequency dependent polarizabilities in regions close to the poles. The change is particularly large for FH because the lowest excitation energy is in much closer agreement with experiment[37] and with the accurate calculation of Dunning[38] (see Table XVII). The only observed excitation energy for FH is reproduced in SOPPA within 0.3 eV whereas the same transition in TDHF is off by 2.0 eV. The SOPPA frequency dependent polarizabilities thus have the resonances in the correct regions but the actual numbers are expected to be off by several per cent owing to the error in the transition moments (see the discussion for He and Be).

We have in Fig. 7 compared the isotropic component of the TDHF and SOPPA polarizabilities with the polarizabilities calculated by Epstein.[12] The coupled Hartree-Fock method used by Epstein is identical to the TDHF approximation and the differences between the two results are caused by the use of limited basis sets in both calculations. The basis set used by Epstein is however smaller than ours which causes the large discrepancies between his length, mixed, and velocity re-
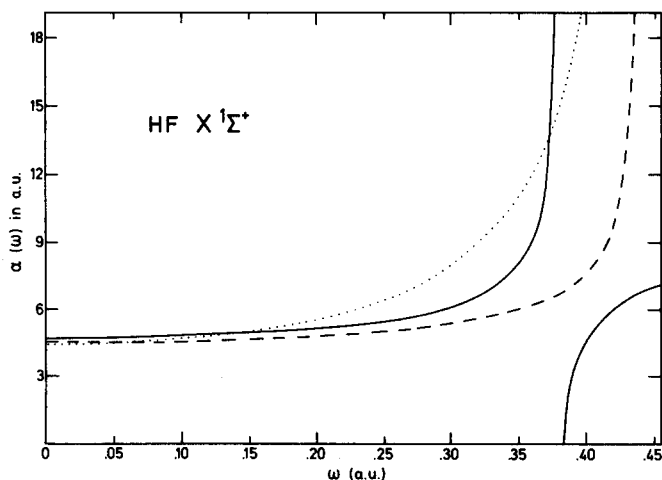

FIG. 7. Same as in Fig. 5 except that this is the isotropic component, $\alpha(\omega) = \frac{1}{3}(2\alpha_\perp(\omega) + \alpha_\parallel(\omega))$. We have compared with the coupled HF result of Epstein[12] (dotted curve).

TABLE XVIII. The isotropic component of the Verdet constant[a] for hydrogen fluoride in units of μmin oersted^{-1} atm^{-1} cm^{-1}.

Wave-length (Å)	TDHF		SOPPA	
	Length	Velocity	Length	Mixed
1000	1.69(+3)	1.71(+3)	1.00(+3)	1.22(+3)
1050	1.70(+6)	1.75(+6)	6.43(+2)	7.76(+2)
1100	1.57(+3)	1.60(+3)	6.79(+2)	8.23(+2)
1150	4.90(+2)	4.90(+2)	1.44(+3)	1.76(+3)
1200	2.67(+2)	2.62(+2)	2.40(+4)	2.97(+4)
1300	1.34(+2)	1.28(+2)	9.17(+2)	1.12(+3)
1400	8.83(+1)	8.28(+1)	2.65(+2)	3.21(+2)
1600	5.09(+1)	4.68(+1)	9.87(+1)	1.17(+2)
2000	2.56(+1)	2.31(+1)	4.01(+1)	4.69(+1)
3000	9.43	8.41	1.33(+1)	1.54(+1)
5000	3.13	2.77	4.08	4.64
10000	7.57(−1)	6.70(−1)	1.01	1.16

[a]At $R = 1.733$ bohr.

sults. A very extensive comparison of various calculations of static polarizabilities has been published by Swanstrøm et al.[39]

We have in Table XVIII reported the Verdet constants for hydrogen fluoride calculated with the Bequerel[14] formula. Since no experimental data are available for FH, it is not possible to determine the r factor in Eq. (1). This implies that the actual numbers in Table XVIII probably are too high but on the basis of our findings for He and CO we expect that the dispersion of the Verdet constant is well reproduced in the present calculation.

III. DISCUSSION

We have demonstrated that polarization propagator approaches offer a direct way to calculate the frequency-dependent polarizabilities, the Verdet constants, and the energy weighted sum rules. The polarization propagator consistent through first order in electronic repulsion is identical to the coupled Hartree–Fock or TDHF method[8] which is a well known and often used approximation for the calculation of second order properties.[40] The polarization propagator which is consistent through *second* order in the electronic repulsion (SOPPA) has also been used to calculate the second order properties. We have shown that the second order polarization propagator approximation gives an improved description of both the frequency-dependent polarizabilities and the Verdet constants, especially in frequency regions close to and above the first excitation threshold. The excitation threshold is located less than 0.5 eV from the experimental values in SOPPA whereas the TDHF excitation energies can be off by a few electron volt. Even though the polarizability in the second order theory is improved compared with the coupled HF result, it still is off by several per cent mainly due to an error in the individual transition moments.

In TDHF and in a complete treatment of the polarization propagator the length, mixed, and velocity representation of the polarizabilities, energy weighted sum rules, and Verdet constants are identical. The larger discrepancies in finite basis set calculations between

the length, mixed, and velocity forms in SOPPA than in TDHF indicates that contributions beyond second order are important for obtaining a really accurate description, not just of the resonances, but also of the overall value of the second order optical properties.

The second order polarization propagator approximation can systematically be extended to a higher order and represents a natural and systematic extension of the coupled HF method. SOPPA can further be interpreted as a consistent way to include important classes of self-energy diagrams[8] and do thus link together many-body diagrammatic[20] and analytical approaches[40] for calculation of second order properties. The discrepancy between the second order theory and experiment is a further indication of the need for going to a higher order approach. A third order propagator theory has previously been described by us[8] and successfully applied to the calculation of individual excitation energies of N_2 by Yeager and Freed.[41] In view of the fact that the first order wavefunction determines the total energy through third order, it is not surprising that self-energy diagrams have to be included through at least third order to obtain accurate results for properties which depend upon the residues (eigenfunctions) of the propagator.

The question of a proper representation of the continuum is an important question in propagator approaches as well as in more conventional methods. Our results for He demonstrates that an improved description of the bound region does not necessarily imply a corresponding improvement in the polarizability. The change in the continuum contribution may neutralize a more accurate description of the terms originating from the bound states.

For Be we have the situation that almost the whole contribution to the polarizability originates from one bound state. The difficulties involved in describing this state also makes it likely that a third order theory improves the polarizability as well.

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