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Computational Aspects of Interaction Hyperpolarizability Calculations. A Study on $H_2\cdots H_2$, Ne···HF, Ne···FH, He···He, Ne···Ne, Ar···Ar, and Kr···Kr[†]

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We report an extensive investigation of the interaction hyperpolarizability of a number of model systems: the hydrogen molecule dimer, the interaction of hydrogen fluoride with a neon atom, and the rare gas diatoms He_2, Ne_2, Ar_2, and Kr_2. Our approach relies on finite-field many-body perturbation theory and coupled cluster calculations. The exploration of the various aspects of interaction hyperpolarizability calculations has brought forth the necessity for well-defined computational strategies that can lead to reliable theoretical predictions for such quantities.

Introduction

Electric hyperpolarizability is an important property of atomic and molecular systems.[1,2] It occupies a central position in the interpretation of nonlinear optical phenomena.[3−7] In recent years a new dimension has been added to electric hyperpolarizability studies through a materials science perspective. The search for new nonlinear optical materials with potential advanced technological applications has emphasized the importance of accurate experimental and theoretical determinations of electric hyperpolarizabilities.[8−11] Important applications of this property have also been reported for the emerging field of simulation studies.[12−14]

Interaction or collisional hyperpolarizability is a relatively new and fascinating subject. Recent experimental work by Donley and Shelton[15] shows that interaction hyperpolarizability is an essential element of the rationalization of nonlinear susceptibility measurements in liquids and solids. Theoretical treatments of interaction hyperpolarizability have been reported by Hunt,[16] Buckingham et al.,[17] and quite recently by Bancewicz.[18] Computational studies have been reported for a number of small systems as He_2, He_3, and Ne_2;[19] He_2,[20] H···H, H···He, and He···He;[21] Ar_2,[22] and He_2, Ar_2.[23,24] The accurate calculation of electric hyperpolarizability is a highly nontrivial matter. A multitude of efforts has been directed by various research groups to the construction of reliable algorithms and computational strategies for the prediction of reliable theoretical values.[25−36] One reasonably expects the appearance of additional complex issues in the calculation of interaction effects.

In this paper, we report results of an explorative investigation on the computational aspects of interaction hyperpolarizability calculations. We have selected a number of model systems and tried to answer the following questions:

(a) What is the size of the interaction effect compared to the hyperpolarizability of the interacting systems?

(b) How important are basis set effects?

(c) If one uses near-Hartree−Fock quality basis sets for the interacting systems, in order to eliminate as much as possible basis set incompleteness from the factors affecting the quality of the predictions, how does the effect vary with the level of theory?

(d) How important is the dependence of the interaction hyperpolarizability on the intermolecular separation for systems as the rare gas diatoms?

The systems chosen for this investigation are $H_2\cdots H_2$, Ne···HF, Ne···FH, He_2, Ne_2, Ar_2, and Kr_2. In all cases we have made a careful choice of basis sets. It is fairly obvious that it makes little sense to attempt calculations of interaction hyperpolarizabilities relying on arbitrarily selected basis sets. We rely on conventional, easily accessible methods for post-Hartree−Fock calculations. There is considerable experience for the performance of hierarchies of Møller−Plesset perturbation theory methods and coupled-cluster techniques in single-system calculations.[37−41] We are interested, for instance, in comparing the known patterns of the convergence of electron correlation effects on the hyperpolarizability of Ne and HF to the emerging ones in the case of the Ne···HF or Ne···FH interaction. Most of the atoms and molecules included in this study have been extensively studied, experimentally or theoretically. Their electric polarizability and hyperpolarizability has been the subject of numerous efforts and the finer points of such calculations are now common knowledge. Consequently, their selection as starting point in this endeavor makes eminent sense.

Theory and Computational Strategy

An uncharged atom or molecule perturbed by a weak, general static electric field is distorted and its symmetry decreases. Adopting Buckingham's conventions, we write the energy and electric moments of the perturbed system in terms of the components of the field as[1,42]

$$\begin{aligned} E &\equiv E(F_\alpha, F_{\alpha\beta}, F_{\alpha\beta\gamma}, F_{\alpha\beta\gamma\delta}, ...) \\ &= E^\circ - \mu_\alpha F_\alpha - ({}^1/_3)\Theta_{\alpha\beta}F_{\alpha\beta} - (1/15)\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma} - \\ &\quad (1/105)\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta} + ... - (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta - \\ &\quad (1/3)A_{\alpha,\beta\gamma}\,F_\alpha F_{\beta\gamma} - (1/6)C_{\alpha\beta,\gamma\delta}\,F_{\alpha\beta}\,F_{\gamma\delta} - \\ &\quad (1/15)E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta} + ... - (1/6)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \\ &\quad (1/6)B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta} + ... - (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + ... \quad (1) \end{aligned}$$

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where F_α, $F_{\alpha\beta}$, etc. are the field, field gradient, etc. at the origin.

$$\begin{aligned}\mu_\alpha &\equiv \mu_\alpha(F_\alpha,F_{\alpha\beta},F_{\alpha\beta\gamma},F_{\alpha\beta\gamma\delta},\ldots)\\ &= \mu_\alpha + \alpha_{\alpha\beta}F_\beta + (1/3)A_{\alpha,\beta\gamma}F_{\beta\gamma} + (1/2)\beta_{\alpha\beta\gamma}F_\beta F_\gamma +\\ &\qquad (1/3)B_{\alpha\beta,\gamma\delta}F_\beta F_{\gamma\delta} + (1/6)\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \ldots\end{aligned} \tag{2}$$

$$\begin{aligned}\Theta_{\alpha\beta} &\equiv \Theta_{\alpha\beta}(F_\alpha,F_{\alpha\beta},F_{\alpha\beta\gamma},F_{\alpha\beta\gamma\delta})\\ &= \Theta_{\alpha\beta} + A_{\gamma,\alpha\beta}E_\gamma + C_{\alpha\beta,\gamma\delta}F_{\gamma\delta} + (1/2)B_{\gamma\delta,\alpha\beta}F_\gamma F_\delta + \ldots\end{aligned} \tag{3}$$

$$\begin{aligned}\Omega_{\alpha\beta\gamma} &\equiv \Omega_{\alpha\beta\gamma}(F_\alpha,F_{\alpha\beta},F_{\alpha\beta\gamma},F_{\alpha\beta\gamma\delta},\ldots)\\ &= \Omega_{\alpha\beta\gamma} + E_{\delta,\alpha\beta\gamma}F_\delta + \ldots\end{aligned} \tag{4}$$

E°, μ_α, $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, and $\Phi_{\alpha\beta\gamma\delta}$ are the energy and the permanent dipole, quadrupole, octopole, and hexadecapole moment of the molecule. The second-, third-, and fourth-order properties are the dipole and quadrupole polarizabilities and hyperpolarizabilities $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$, $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$, and $B_{\alpha\beta,\gamma\delta}$. The subscripts denote Cartesian components and a repeated subscript implies summation over x, y, and z. The number of independent components needed to specify electric multipole moment and polarizability tensors depends on the symmetry of the system.[1]

Our computational approach relies on the finite-field method.[43] When the perturbing field is weak enough, the expansions in eqs 1−4 display satisfactory convergence and the electric properties of interest can be determined from either the energy or the induced multipole moments.[44−50] In this work, all properties are extracted from finite-field self-consistent field (SCF), Møller−Plesset perturbation theory (MP) and coupled-cluster techniques (CC). Detailed presentations of these methods can be found in standard references and textbooks.[51−57] MP methods are relatively inexpensive compared to the more time-consuming CC techniques. In the MP4 method the energy is defined as

$$\mathrm{MP4} = \mathrm{SCF} + \mathrm{D2} + \mathrm{D3} + \mathrm{S4} + \mathrm{D4} + \mathrm{T4} + \mathrm{Q4} + \mathrm{R4} \tag{5}$$

The fourth-order terms in eq 5 are contributions from single (S4), double (D4), triple (T4), and quadruple (Q4) substitutions from the reference wave function and R4 is the renormalization term. By analogy, we assume similar partitions for all properties calculated at this level of property. Two lower-order MP methods are also used in this work: MP2 and the partial fourth-order SDQ-MP4 method. These constitute especially useful alternatives in cases where even the MP4 method is not accessible and are defined as

$$\begin{gathered}\mathrm{MP2} = \mathrm{SCF} + \mathrm{D2}\\ \text{SDQ-MP4} = \mathrm{SCF} + \mathrm{D2} + \mathrm{D3} + \mathrm{S4} + \mathrm{D4} + \mathrm{Q4} + \mathrm{R4}\end{gathered} \tag{6}$$

The most accurate methods employed are CCSD, single and double excitation coupled-cluster theory and CCSD(T), which includes an estimate of connected triple excitations by a perturbational treatment.

In general, an interaction property of A···B may be defined as

$$P_{\mathrm{int}} = P(\mathrm{A}\cdots\mathrm{B}) - P(\mathrm{A}) - P(\mathrm{B}) \tag{7}$$

Equation 7 should provide an accurate picture of the interaction of the two subsystems if large, flexible, and suitably optimized basis sets are used in the calculations. It is not always clear how these requirements are met in hyperpolarizability calculations. Or, to be more explicit, it is still not clear how basis set incompleteness in the calculation of P(A) or P(B) influences the accuracy of the interaction quantity P_{int}. We lean heavily on the counterpoise correction (CP) method to eliminate basis set superposition errors (BSSE) from our calculations. Instead of using P(A) and P(B) in eq 7, we replace them by P(A···X) and P(X···B). P(A···X) is the value of property P for subsystem A in the presence of the ghost orbitals of subsystem B. Thus

$$P_{\mathrm{int}} = P(\mathrm{A}\cdots\mathrm{B}) - P(\mathrm{A}\cdots\mathrm{X}) - P(\mathrm{X}\cdots\mathrm{B}) \tag{8}$$

The adoption of eq 8 entails a dramatic increase of the computational effort. It is an essential part of this investigation to collect computational experience on the following points: (a) the convergence of P(A···X) to P(A) with basis set size;

(b) the size of the error lurking in interaction property calculations performed with reasonably large basis set but estimated assuming the validity of eq 7, that is, ignoring BSSE effects.

Basis Set Construction and Computational Details

All basis sets used in this work have been especially designed for electric polarizability calculations. We follow a computational philosophy presented in detail in previous work.[39−41,58−60] For molecules with H, C, N, O, and F atomic centers our approach can be summarized in three steps:

(a) A reliable initial substrate is augmented with diffuse Gaussian-type functions (GTF), s-GTF for H and s-, p-GTF for C, N, O, and F.

(b) The resulting basis set is augmented with relatively tight p-GTF for H and d-GTF for C, N, O, and F. The exponents of the GTF are chosen to minimize the energy of the free molecule, E°.

(c) In a last step, we add diffuse p-GTF on H and d-GTF on C, N, O, and F with exponents chosen to maximize the mean dipole polarizability $\bar{\alpha}$.

For He, Ne, Ar, and Kr the construction follows a somewhat more elaborate route. The addition of diffuse GTF to the substrate is followed by the optimization of GTF exponents for the dipole polarizability (p-GTF for He, d-GTF for Ne, Ar, and Kr) and the quadrupole polarizability (d-GTF for He, f-GTF for Ne, Ar, and Kr).

5D and 7F GTF were used in all basis sets.

The designed basis sets are expected to predict accurate electric properties for the molecules of interest in this work. The global quality of such basis sets has been tested in a large variety of systems.[39−41,48−50,58−61] What is considered to be a very good basis set for electric polarizability and hyperpolarizability calculations on an isolated molecule should be accepted as no more than a starting point for the reliable prediction of interaction or collisional quantities.

All calculations were performed with GAUSSIAN 92[62] and GAUSSIAN 94.[63]

Atomic units are used throughout this paper. Conversion factors to SI units are as follows: energy, $1\ E_\mathrm{h} = 4.359\,7482 \times 10^{-18}$ J; length, $1\ a_0 = 0.529\,177\,249 \times 10^{-10}$ m; dipole moment, μ, $1\ \mathrm{e\ a_0} = 8.478\,358 \times 10^{-30}$ C m; dipole polarizability, α, $1\ \mathrm{e^2\ a_0^2\ E_h^{-1}} = 1.648\,778 \times 10^{-41}\ \mathrm{C^2\ m^2\ J^{-1}}$; first dipole hyperpolarizability, β, $1\ \mathrm{e^3\ a_0^3\ E_h^{-2}} = 3.206\,361 \times 10^{-53}\ \mathrm{C^3\ m^3\ J^{-2}}$; second dipole hyperpolarizability, γ, $1\ \mathrm{e^4\ a_0^4\ E_h^{-3}}$

TABLE 1: Interaction[a] Polarizability and Hyperpolarizability of the H_2 in the T-shaped Configuration Calculated with Basis Set [6s4p1d] at the CCSD(T) Level of Theory

property	H_2-H_2	H_2-X	$X-H_2$	H_2	P_{int}
α_{xx}	11.2636	6.7758	4.7232		−0.2354
α_{yy}	9.2791	4.7265	4.7230		−0.1704
α_{zz}	11.9657	4.7261	6.7760		0.4636
$\bar{\alpha}^b$	10.8361	5.4095	5.4074	5.4068	0.0192
γ_{xxxx}	1265	763	604		−102
γ_{yyyy}	1157	635	603		−81
γ_{zzzz}	1607	632	765		210
γ_{xxyy}	405	234	202		−31
γ_{yyzz}	437	204	234		−1
γ_{zzxx}	461	233	235		−7
$\bar{\gamma}^b$	1327	675	662	659	−10

[a] The interaction property is defined as $P_{int} = P(H_2-H_2) - P(H_2\text{-}X) - P(X-H_2)$. One H_2 is on the x axis with the mid-bond point at the origin and the other on the positive z axis. The distance of the two mid-bond points is 6.5 a_0. [b] $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ and $\bar{\gamma} = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})/5$.

TABLE 2: Interaction[a] Polarizability and Hyperpolarizability of the H_2 in the Linear Configuration[b] Calculated with Basis Set [6s4p1d] at the CCSD(T) Level of Theory

property	H_2-H_2	H_2-X	H_2	P_{int}
α_{zz}	14.3370	6.7750	6.7761	0.7870
α_{xx}	9.2535	4.7233	4.7222	−0.1931
$\bar{\alpha}$	10.9480	5.4072	5.4068	0.1336
$\Delta\alpha$	5.0835	2.0517	2.0539	0.9801
γ_{zzzz}	1951	766	764	418
γ_{xxxx}	1112	599	598	−87
γ_{xxzz}	467	233	234	0.5
$\bar{\gamma}$	1356	659	659	38
$\Delta_1\gamma$	2806	602	604	1603
$\Delta_2\gamma$	262	−33	−45	329

[a] The interaction property is defined as $P_{int} = P(H_2-H_2) - 2P(H_2-X)$. One H_2 is on the z axis with the mid-bond point at the origin and the other on the positive z axis. The distance of the two mid-bond points is 6.5 a_0. [b] The mean and anisotropy of the polarizability is defined as $\bar{\alpha} = (\alpha_{zz} + 2\alpha_{xx})/3$ and $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$. For the hyperpolarizability $\bar{\gamma} = (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15$, $\Delta_1\gamma = 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz}$, and $\Delta_2\gamma = \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz}$.

$= 6.235\,378 \times 10^{-65}$ C^4 m^4 J^{-3}; quadrupole polarizability, C, 1 $e^2 a_0^4 E_h^{-1} = 4.617\,048 \times 10^{-62}$ C^2 m^4 J^{-1}.

Results and Discussion

$H_2\cdots H_2$. Following Røeggen and Wind,[64] we have studied two configurations of the hydrogen molecule dimer. In both the T-shaped and linear configuration the distance of the two mid-bond points is fixed at 6.5 a_0. The H_2 bond length is fixed at 1.449 a_0. Two basis sets were optimized on the H_2 subsytem. Basis A ≡ (8s3p1d)[6s3p1d] is built upon a (6s)[4s] substrate[65] along the lines specified in the previous section. Basis B ≡ [6s4p1d] contains an additional diffuse p-GTF. Full results at the CCSD(T) level of theory for the $(H_2)_2$ system and the monomer are given in Table 1 for the T-shaped form and Table 2 for the linear one. All MO were included in the correlated calculations. Results are given as $\alpha_{\alpha\beta}/e^2 a_0^2 E_h^{-1}$ and $\gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$.

Basis set B gives $\bar{\alpha} = 5.4068$ and $\bar{\gamma} = 659$, which compare well with the experimental values of 5.428[29] and 686 ± 4,[30] respectively. Examining the entries for H_2-X, $X-H_2$, and H_2 in Table 1, we see that the presence of ghost orbitals affects mostly the H_2-X results. But even if the differences between the three abovementioned columns are small, neglect of BSSE effects entails sizable errors for P_{int}. This is most obvious for $\bar{\gamma}$: for H_2-X, H_2-X, and H_2 we obtain 675, 662, and 659, respectively. The three numbers are quite close, differences not exceeding a few percent. But these differences are very important when compared to the interaction hyperpolarizability $\bar{\gamma}_{int} = -10$. Another important observation concerns the interaction effects on the components of $\gamma_{\alpha\beta\gamma\delta}$. The effect is highly anisotropic. The interaction quantity is negative for both γ_{xxxx} and γ_{yyyy} but strongly positive for γ_{zzzz}.

TABLE 3: Electron Correlation Effects on the Interaction[a] Electric Properties[b] of Ne−HF

property	method	Ne	X−Ne	FH	FH−X	FH−Ne	P_{int}
μ_z	SCF	0	−0.0001	0.7592	0.7592	0.7906	0.0315
	MP2	0	−0.0001	0.7082	0.7081	0.7429	0.0349
	SDQ-MP4	0	−0.0001	0.7074	0.7074	0.7415	0.0342
	MP4	0	−0.0001	0.6986	0.6986	0.7334	0.0349
	CCSD	0	−0.0001	0.7098	0.7098	0.7434	0.0337
	CCSD(T)	0	−0.0001	0.7034	0.7034	0.7375	0.0342
$\bar{\alpha}$	SCF	2.3676	2.3678	4.9014	4.9020	7.2883	0.0185
	MP2	2.7212	2.7217	5.7106	5.7117	8.4579	0.0245
	SDQ-MP4	2.6806	2.6809	5.6152	5.6161	8.3246	0.0276
	MP4	2.7464	2.7468	5.7972	5.7983	8.5738	0.0287
	CCSD	2.6581	2.6585	5.5483	5.5491	8.2366	0.0290
	CCSD(T)	2.7020	2.7024	5.6651	5.6660	8.4002	0.0318
$\bar{\beta}$	SCF	0	0.01	−5.66	−5.66	−4.23	1.42
	MP2	0	0.01	−7.22	−7.24	−4.91	2.32
	SDQ-MP4	0	0.01	−7.46	−7.47	−5.24	2.22
	MP4	0	0.02	−8.38	−8.40	−5.85	2.53
	CCSD	0	0.01	−6.98	−6.99	−4.89	2.09
	CCSD(T)	0	0.01	−7.50	−7.51	−5.24	2.26
$\bar{\gamma}$	SCF	67.5	68.0	305.5	305.8	366.6	−7.2
	MP2	110.1	110.4	531.2	532.2	630.3	−12.3
	SDQ-MP4	108.3	107.7	525.8	528.0	625.8	−9.9
	MP4	119.8	121.0	604.3	606.1	719.2	−7.9
	CCSD	102.6	95.0	493.6	491.0	590.6	4.6
	CCSD(T)	108.5	103.9	540.4	539.3	638.4	−4.8

[a] Interaction property defined as $P_{int} = P(\text{Ne}-\text{HF}) - P(\text{X}-\text{HF}) - P(\text{Ne}-\text{X})$. Basis set Ne = [9s6p5d4f], F = [9s6p5d3f], and H = [6s3p1d]. [b] The mean first dipole hyperpolarizability is defined as $\bar{\beta} = (3/5)(\beta_{zxx} + \beta_{zyy} + \beta_{zzz})$.

TABLE 4: Electron Correlation Effects on the Interaction[a] Electric Properties of Ne−FH

property	method	Ne	Ne−X	FH	X−FH	Ne−FH	P_{int}
μ_z	SCF	0	0.0001	0.7592	0.7592	0.7687	0.0094
	MP2	0	0.0001	0.7082	0.7082	0.7180	0.0097
	SDQ-MP4	0	0.0001	0.7074	0.7074	0.7172	0.0097
	MP4	0	0.0001	0.6986	0.6986	0.7084	0.0097
	CCSD	0	0.0001	0.7098	0.7098	0.7195	0.0096
	CCSD(T)	0	0.0001	0.7034	0.7035	0.7131	0.0095
$\bar{\alpha}$	SCF	2.3676	2.3679	4.9014	4.9015	7.2741	0.0047
	MP2	2.7212	2.7217	5.7106	5.7109	8.4386	0.0060
	SDQ-MP4	2.6806	2.6809	5.6152	5.6152	8.3047	0.0086
	MP4	2.7464	2.7468	5.7972	5.7974	8.5533	0.0091
	CCSD	2.6581	2.6585	5.5483	5.5483	8.2155	0.0087
	CCSD(T)	2.7020	2.7024	5.6651	5.6652	8.3775	0.0099
$\bar{\beta}$	SCF	0	−0.01	−5.66	−5.67	−5.96	−0.28
	MP2	0	0.00	−7.22	−7.25	−7.64	−0.39
	SDQ-MP4	0	−0.01	−7.46	−7.48	−7.86	−0.37
	MP4	0	0.00	−8.38	−8.41	−8.83	−0.42
	CCSD	0	0.00	−6.98	−7.00	−7.37	−0.37
	CCSD(T)	0	0.00	−7.50	−7.53	−7.92	−0.39
$\bar{\gamma}$	SCF	67.5	68.0	305.5	305.8	368.3	−5.5
	MP2	110.1	111.5	531.2	532.3	643.5	−0.3
	SDQ-MP4	108.3	109.0	525.8	525.1	632.5	−1.6
	MP4	119.8	121.3	604.3	599.1	692.7	−27.7
	CCSD	102.6	98.7	493.6	485.9	604.2	19.6
	CCSD(T)	108.5	105.7	540.4	538.7	680.9	36.5

[a] Interaction property defined as $P_{int} = P(\text{Ne}-\text{FH}) - P(\text{X}-\text{FH}) - P(\text{Ne}-\text{X})$. Basis set Ne = [9s6p5d4f], F = [9s6p5d3f], and H = [6s3p1d].

The interaction polarizability and hyperpolarizability is larger for the linear configuration. We observe a very important, positive effect for the longitudinal component γ_{zzzz} and a less important but negative effect for the transversal one. The overall

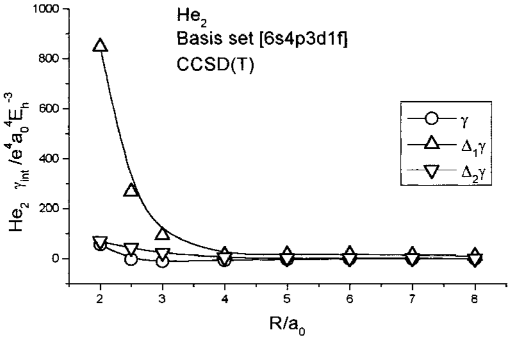

Figure 1. Interaction hyperpolarizability of two helium atoms.

TABLE 5: SCF Interaction Polarizability and Hyperpolarizability of Two He Atoms Calculated with the 13s11p7d3f Basis Set

R/a_0	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
2.0	−0.1490	0.7526	39.36	623.64	47.41
2.5	−0.1940	0.2888	−3.86	194.98	32.12
3.0	−0.1297	0.1555	−10.12	62.90	16.59
4.0	−0.0349	0.0986	−6.05	6.76	2.36
5.0	−0.0066	0.0705	−2.10	9.85	0.24
6.0	−0.0009	0.0464	−0.54	12.04	0.50
7.0	−0.0001	0.0303	−0.11	10.19	0.49
8.0	0.0000	0.0205	−0.01	7.55	0.35

TABLE 6: Basis Set Effects on the Interaction Polarizability and Hyperpolarizability of Two He Atoms at the CCSD(T) Level of Theory

	$\bar{\alpha}$		$\Delta\alpha$		$\bar{\gamma}$	
R/a_0	[6s4p3d]	[6s4p3d1f]	[6s4p3d]	[6s4p3d1f]	[6s4p3d]	[6s4p3d1f]
2.0	−0.1312	−0.1307	0.8365	0.8361	56.13	56.35
2.5	−0.1994	−0.1989	0.3201	0.3196	−2.56	−2.62
3.0	−0.1357	−0.1352	0.1753	0.1749	−11.63	−11.52
4.0	−0.0352	−0.0349	0.1137	0.1135	−7.07	−6.96
5.0	−0.0056	−0.0054	0.0808	0.0808	−2.31	−2.25
6.0	−0.0003	−0.0002	0.0528	0.0529	−0.52	−0.32
7.0	0.0003	0.0004	0.0343	0.0342	−0.18	−0.13
8.0	0.0002	0.0003	0.0229	0.0230	−0.05	0.06

TABLE 7: Cartesian Components, Mean, and Anisotropy of the Interaction Hyperpolarizability of Two He Atoms. CCSD(T) Results Calculated with a [6s4p3d1f] Basis Set

R/a_0	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}	$\bar{\gamma}$	$\Delta_1\gamma$	$\Delta_2\gamma$
2.0	233.64	−18.52	24.38	56.35	848.14	68.84
2.5	57.96	−24.39	−1.51	−2.62	266.91	42.63
3.0	11.05	−18.60	−4.89	−11.52	92.04	22.00
4.0	−3.15	−8.08	−2.51	−6.96	15.34	3.83
5.0	1.10	−3.73	−0.60	−2.25	16.42	0.97
6.0	3.14	−1.92	0.10	−0.32	17.40	0.62
7.0	2.71	−1.42	0.10	−0.13	14.11	0.69
8.0	2.16	−0.96	0.16	0.06	10.80	0.24

effect is $\bar{\gamma}_{int} = 38$ for the mean hyperpolarizability. The highly anisotropic character of the interaction is evidenced by the very large $\Delta_1\gamma$ and $\Delta_2\gamma$ values. It is also worth observing that the $\gamma_{\alpha\beta\gamma\delta}$ values for H_2−X and H_2 are quite close, indicating a small BSSE for the linear configuration.

We do no present here full results for basis A. For the T-shaped configuration we find $\bar{\alpha}_{int} = 0.0199$ and $\bar{\gamma}_{int} = -2$. For the linear configuration $\bar{\alpha}_{int} = 0.9752$ and $\bar{\gamma}_{int} = 48$. In both cases the predictions are very similar. In fact, we observe a closer agreement for the interaction quantities than that obtained for the properties of H_2.

Ne···HF, Ne···FH. The interaction of neon with hydrogen fluoride has attracted some attention.[66−68] We adopt the findings of the excellent study of Oneil et al.[67] for the two stable geometries of the complex. The system is linear with z as the molecular axis. The center of mass of FH is at the origin with the hydrogen on the positive axis. The FH bond length is fixed at 1.7328 a_0.[69] In the most stable Ne···HF configuration the neon atom lies on the positive z axis, at a distance of 6.25 a_0. For Ne···FH the neon atom lies at −5.96 a_0 on the negative z axis. The basis sets used are [9s6p5d4f] for Ne, [9s6p5d3f] for F, and [6s3p1d] for H, built upon substrates of (13s7p)[7s4p] for F, Ne, and (6s)[4s] for H.[65] The innermost MO was kept frozen in all correlated calculations on Ne or HF. The two innermost MO were kept frozen on all correlated calculations on the complex.

The results are displayed in Tables 3 and 4. We show SCF, MP2, SDQ-MP4, MP4, CCSD, and CCSD(T) values for μ_z/ea_0, $\bar{\alpha}/e^2a_0^2E_h^{-1}$, $\bar{\beta}/e^3a_0^3E_h^{-2}$ and $\bar{\gamma}/e^4a_0^4E_h^{-3}$. Let us consider first the results obtained for the monomers. For Ne we obtain, at the CCSD(T) level of theory, $\bar{\alpha} = 2.7020$ and $\bar{\gamma} = 108.5$, to be compared to the experimental values of 2.669[70] and 108.[30] For HF, at the same level of theory, we obtain $\mu_z = 0.7034$, $\bar{\alpha} = 5.6651$, $\bar{\beta} = -7.51$, and $\bar{\gamma} = 540.4$. Rozyczko and Bartlet[71] reported EOM-CC (equation of motion CC) values of $\bar{\beta} = -7.92$ and $\bar{\gamma} = 558$ calculated with a t-aug-cc-pVTZ basis set. The quality of the basis set used for HF may further be judged by the agreement of our MP4 results with those obtained (in parentheses) by Papadopoulos et al.[72] with a large (13s8p7d5f/10s7p5d) basis set: $\mu_z = 0.6986$ (0.699), $\bar{\alpha} = 5.80$ (5.74), $\bar{\beta} = -8.4$ (−8.32), and $\bar{\gamma} = 604$ (578).

The post-Hartree−Fock results for the interaction dipole moment and dipole polarizability are quite stable. The effect is rather small for both configurations. The $\bar{\beta}_{int}$ is larger for the FH−Ne configuration. For Ne−FH it is of the opposite sign and rather small. We concentrate on the second hyperpolarizability. The calculation of this property for either Ne or HF has absorbed increased amounts of computational efforts. In both systems electron correlation changes drastically the SCF picture of the system. We find that $\bar{\gamma}_{int}$ is quite small compared to electron correlation effects for Ne or HF. We obtain $\bar{\gamma}_{int}$(Ne−HF) = −4.8 and $\bar{\gamma}_{int}$(Ne−FH) = 36.5 at the CCSD(T) level of theory. Thus, for $\bar{\gamma}_{int}$(Ne−HF) the SCF result of −7.2 changes little upon the inclusion of electron correlation. The difficulty of predicting even the sign of $\bar{\gamma}_{int}$ is obvious: the CCSD result is positive while the presumably more accurate CCSD(T) methods yield a negative value. For the Ne−FH configuration, $\bar{\gamma}_{int}$ is again negative and relatively small, close to the Ne−HF one. The fourth-order SDQ-MP4 and MP4 $\bar{\gamma}_{int}$ are −1.6 and −27.7. At CCSD and CCSD(T) we obtain 19.6 and 36.5. The

TABLE 8: Analysis of Electron Correlation Effects[a] on the Mean Interaction Hyperpolarizability of Two He Atoms

R/a_0	SCF	D2	D3	S4	D4	T4	QR4	MP4	ΔCCSD	T	CCSD(T)
2.0	39.93	12.24	0.87	1.04	0.75	0.87	−0.67	55.06	15.13	1.27	56.35
2.5	−3.72	0.99	−0.28	0.20	−0.17	0.28	−0.07	−2.82	0.66	0.45	−2.62
3.0	−10.09	−0.93	−0.37	0.03	−0.24	0.15	0.00	−11.44	−1.69	0.26	−11.52
4.0	−6.03	−0.69	−0.07	0.05	−0.15	0.08	0.01	−6.83	−1.04	0.14	−6.96
5.0	−2.11	−0.14	−0.12	0.05	−0.05	0.04	−0.02	−2.34	−0.21	0.07	−2.25
6.0	−0.56	0.03	0.05	0.06	−0.05	0.02	−0.01	−0.43	0.21	0.03	−0.32
7.0	−0.12	0.05	−0.10	−0.02	0.05	0.01	−0.01	−0.14	−0.02	0.01	−0.13
8.0	−0.03	0.02	0.00	−0.11	0.04	0.00	0.00	−0.06	0.08	0.01	0.06

[a] CCSD(T) = ΔCCSD + T. Basis Set [6s4p3d1f].

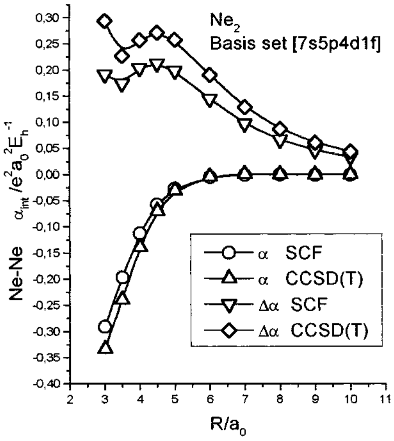

Figure 2. Mean and anisotropy of the interaction polarizability of two neon atoms.

TABLE 9: Mean and Anisotropy of the Interaction Polarizability of Two Ne Atoms Calculated at the SCF, CCSD, and CCSD(T) Level of Theory with a [7s5p4d1f] Basis Set

	$\bar{\alpha}$			$\Delta\alpha$		
R/a_0	SCF	CCSD	CCSD(T)	SCF	CCSD	CCSD(T)
3.0	−0.2899	−0.3262	−0.3327	0.1919	0.2839	0.2945
3.5	−0.1958	−0.2322	−0.2384	0.1744	0.2224	0.2273
4.0	−0.1118	−0.1347	−0.1383	0.2037	0.2515	0.2575
4.5	−0.0567	−0.0679	−0.0693	0.2126	0.2645	0.2720
5.0	−0.0261	−0.0300	−0.0302	0.1985	0.2500	0.2580
6.0	−0.0042	−0.0035	−0.0029	0.1446	0.1845	0.1911
7.0	−0.0002	0.0008	0.0013	0.0974	0.1246	0.1289
8.0	0.0002	0.0008	0.0010	0.0662	0.0845	0.0874
9.0	0.0001	0.0003	0.0005	0.0465	0.0592	0.0613
10.0	0.0000	0.0002	0.0003	0.0339	0.0430	0.0444

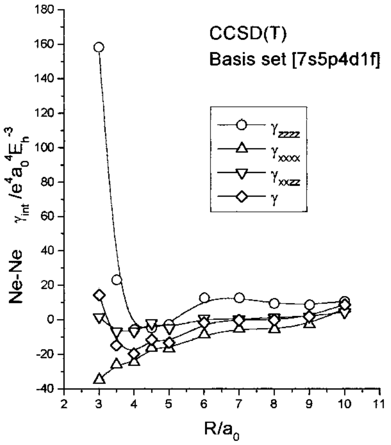

Figure 3. Cartesian components and mean of the interaction hyperpolarizability of two neon atoms.

TABLE 10: Mean and Anisotropy of the Interaction Hyperpolarizability of Two Ne Atoms Calculated at the SCF and CCSD(T) Level of Theory with a [7s5p4d1f] Basis Set

	$\bar{\gamma}$		$\Delta_1\gamma$		$\Delta_2\gamma$	
R/a_0	SCF	CCSD(T)	SCF	CCSD(T)	SCF	CCSD(T)
3.0	1.8	14.5	240.6	618.6	57.1	113.1
3.5	−13.4	−14.6	48.6	152.8	18.3	38.1
4.0	−13.0	−19.6	4.7	61.9	3.2	9.9
4.5	−9.9	−11.3	3.8	45.0	−1.3	−8.8
5.0	−6.5	−13.1	14.1	44.0	−1.6	9.3
6.0	−2.1	−1.6	30.4	74.6	0.1	−0.1
7.0	−0.6	−0.2	29.6	59.6	2.4	6.8
8.0	0.0	−0.2	23.8	53.7	1.4	−3.1
9.0	0.1	2.0	17.5	42.2	0.0	−5.3
10.0	0.0	8.9	12.5	19.4	0.9	−8.7

TABLE 11: Mean and Anisotropy of the Interaction Polarizability of Two Ar Atoms[a]

	$\bar{\alpha}$			$\Delta\alpha$		
R/a_0	SCF	D2	MP2	SCF	D2	MP2
3.5	1.5679	0.8940	2.4619	13.7622	2.3866	16.1488
4.0	−0.2565	0.2663	0.0098	6.9311	0.9881	7.9192
4.5	−0.5354	0.1016	−0.4337	4.5292	0.5811	5.1103
5.0	−0.4567	0.0536	−0.4031	3.4776	0.4316	3.9093
6.0	−0.1816	0.0380	−0.1436	2.4835	0.3165	2.8000
7.0	−0.0404	0.0303	−0.0101	1.8219	0.2327	2.0546
8.0	0.0008	0.0190	0.0198	1.3083	0.1598	1.4681
9.0	0.0065	0.0105	0.0168	0.9395	0.1085	1.0480
10.0	0.0047	0.0057	0.0104	0.6878	0.0760	0.7639
11.0	0.0029	0.0031	0.0061	0.5164	0.0554	0.5719
12.0	0.0018	0.0018	0.0034	0.3972	0.0417	0.4389

[a] Analysis of MP2 results obtained with basis set [8s6p5d4f].

results are again relatively small in absolute terms. Overall, in absolute terms, $\bar{\gamma}_{int}$ is ≈ 1% of the $\bar{\gamma}$(Ne−HF) value and ≈5% of $\bar{\gamma}$(Ne−FH).

He···He. The interaction hyperpolarizability of two helium atoms was studied at the SCF level by Papadopoulos and Waite[19] more than a decade ago. MP4 results were recently reported by Bishop and Dupuis.[20] An elegant treatment of the problem by Li et al.[31] produced new equations for the long-range interaction induced hyperpolarizability. We extend the investigation to higher levels of theory and include a study of basis set effects.

We have used an uncontracted (10s) substrate[73] to construct a very large (13s11p7d3f) basis set for He. This basis yields SCF values $\alpha/e^2a_0^2E_h^{-1} = 1.3222$ and $\gamma/e^4a_0^4E_h^{-3} = 36.0$. The numerical Hartree−Fock values of Stiehler and Hinze[74] are 1.32223 and 36.1. SCF dipole polarizability and hyperpolarizability mean and anisotropy values for internuclear separations R/a_0 = 2, 2.5, 3, 4, 5, 6, 7, and 8 of the helium diatom are given in Table 5. It is obvious from the displayed values that the effect is strongly anisotropic for both $\alpha_{\alpha\beta}$ and $\gamma_{\alpha\beta\gamma\delta}$. The interaction quantities are dominated by the axial component of the polarizability and hyperpolarizability tensors. The anisotropy of the hyperpolarizability $\Delta_1\gamma_{int}$ is significant even for large internuclear separations where $\bar{\gamma}_{int}$ is almost negligible. This will emerge as a recurring pattern in all rare gas diatoms.

Two additional basis sets for He were obtained from a (6s)-[4s] substrate,[65] [6s4p3d] and [6s4p3d1f]. Both were used in MP and CC calculations. In Table 6 we list the basis set effect on $\bar{\alpha}$, $\Delta\alpha$, and $\bar{\gamma}$ at the CCSD(T) level of theory. The presence of the f-GTF has a small but not altogether negligible effect on the interaction quantities. A full description of the interaction hyperpolarizability is given in Table 7. The most important conclusion from the entries in Table 7 is the radically different behavior of the longitudinal and transversal components. This results in very large anisotropies for the short and medium range. A more eloquent picture of the effect is presented in Figure 1. Last, a complete analysis of electron correlation effects on the mean interaction hyperpolarizability $\bar{\gamma}_{int}$ is given in Table 8. A comparison of the MP4 and CCSD(T) values for this quantity shows small but nonnegligible differences between the two methods.

Ne···Ne. Our work on the neon diatom is part of a more general effort on Ne$_n$ clusters. Several basis sets have been designed for calculations of collisional properties of such systems.[75] We have used a small but flexible [7s5p4d1f] basis set built upon a (11s6p)[5s3p] TZV substrate.[76] In Table 9 we show the interaction polarizability results at the SCF, CCSD, and CCSD(T) levels of theory. In Figure 2 we have plotted the

TABLE 12: Cartesian Components and Mean Value of the Interaction Second Hyperpolarizability of Two Ar Atoms[a]

	γ_{zzzz}			γ_{xxxx}			γ_{xxzz}			$\bar{\gamma}$		
R/a_0	SCF	D2	MP2	SCF	D2	MP2	SCF	D2	MP2	SCF	D2	MP2
3.5	19463.9	11237.1	30701.0	−78.7	278.9	200.1	1815.0	1251.7	3066.7	5302.8	3397.5	8700.3
4.0	4935.4	2664.6	7599.9	−450.3	−62.2	−512.5	221.1	203.6	424.8	923.7	662.7	1586.5
4.5	1895.2	1024.1	2919.4	−408.2	−89.7	−497.9	−20.0	49.5	29.5	145.3	196.6	341.9
5.0	860.5	501.3	1361.9	−348.1	−88.0	−436.0	−67.0	9.8	−57.2	−67.1	61.2	−5.9
6.0	290.0	213.7	503.8	−250.6	−68.8	−319.2	−51.7	−0.4	−52.1	−116.9	5.7	−111.2
7.0	239.0	158.0	397.0	−179.3	−51.2	−230.5	−22.5	2.6	−19.7	−65.8	6.5	−59.3
8.0	240.3	130.4	370.7	−129.4	−36.6	−166.0	−4.6	4.6	−0.2	−24.7	10.3	−14.5
9.0	211.0	99.3	310.3	−95.3	−29.5	−124.9	2.4	4.5	6.9	−6.8	7.8	1.0
10.0	169.2	74.1	243.4	−71.9	−22.0	−93.9	4.4	4.7	9.2	−0.9	6.9	6.0
11.0	130.7	51.1	181.7	−55.2	−17.2	−72.3	4.7	3.3	8.0	0.6	3.7	4.2
12.0	100.3	39.6	140.1	−43.6	−13.8	−57.4	4.2	2.7	6.9	0.3	2.7	3.0

[a] Analysis of MP2 results obtained with basis set [8s6p5d4f].

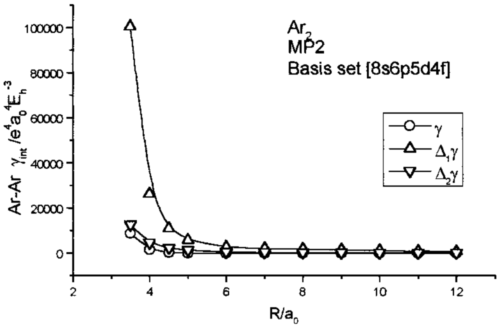

Figure 4. Interaction hyperpolarizability of two argon atoms.

TABLE 13: Mean and Anisotropy of the Interaction Polarizability of Two Kr Atoms[a]

	$\bar{\alpha}$			$\Delta\alpha$		
R/a_0	SCF	D2	MP2	SCF	D2	MP2
4.0	2.4113	1.2014	3.6127	21.8086	3.0283	24.8369
4.5	−0.0162	0.5147	0.4985	12.5612	1.5374	14.0985
5.0	−0.5513	0.2743	−0.2770	8.6870	0.9826	9.6696
5.5	−0.5518	0.1780	−0.3738	6.7438	0.7404	7.4842
6.0	−0.4061	0.1359	−0.2702	5.5905	0.6154	6.2058
7.0	−0.1350	0.0944	−0.0406	4.1056	0.4533	4.5589
8.0	−0.0157	0.0612	0.0455	3.0268	0.3160	3.3428
9.0	0.0147	0.0352	0.0499	2.2178	0.2108	2.4286
10.0	0.0153	0.0192	0.0345	1.6388	0.1423	1.7811
11.0	0.0105	0.0105	0.0209	1.2338	0.0999	1.3338
12.0	0.0065	0.0058	0.0123	0.9489	0.0734	1.0224

[a] Analysis of MP2 results obtained with basis set [8s7p6d5f].

mean and the anisotropy of the interaction property against the internuclear separation. The magnitude of $\bar{\alpha}_{int}$ and $\Delta\alpha_{int}$ is comparable at short range. The anisotropy remains nonnegligible even for relatively large R/a_0 values. It is worth noticing the shape of $\Delta\alpha_{int}$ in $3 \le R/a_0 \le 5$. The difference between CCSD(T) and CCSD is visible for the anisotropy, even at large internuclear separations. The interaction quantities for $\bar{\gamma}$, $\Delta_1\gamma$, and $\Delta_2\gamma$ are given in Table 10, while the Cartesian components are plotted in Figure 3. We observe again the emergence of the now familiar pattern. The axial part of the interaction dominates the total effect. The interaction hyperpolarizability anisotropy is quite important for the whole range of internuclear separations considered. Numerical instabilities have also been observed in the range $7 \le R/a_0 \le 10$. These concern the property values obtained for Ne−X. It is not quite sure how the total picture of the effect will change with the use of larger basis sets and levels of theory higher than CCSD(T). Last, we observe the importance of correlation effects for all internuclear separations considered in this work, but more so in the range $3 \le R/a_0 \le 6$.

Summarizing our experience on the collisional properties of the neon diatom we want to record the following. Electron correlation effects are already very important for the Ne atom.[77] We expect this computational aspect to be even more important for Ne$_2$. One should also keep in mind that Ne$_2$ and Ne−X represent different types of problems but the interaction properties are obtained as differences P(Ne−Ne) − 2P(Ne−X). Thus, the accurate determination of P_{int} might be influenced by a number of factors not always easy to bring under control. What is more, the relative importance of computational aspects may change with the internuclear separation.

Ar···Ar. We have constructed a [8s6p5d4f] basis set for Ar, starting from an initial TZV (15s9p)[6s4p] basis set. This basis set gives for Ar $\alpha/e^2a_0{}^2E_h{}^{-1} = 10.66$, $\alpha_2/e^2a_0{}^4E_h{}^{-1} = 49.70$ and $\gamma/e^4a_0{}^4E_h{}^{-3} = 942$ at the SCF level. The NHF[74,76] values are 10.758, 50.21, and 966. Our SCF values are only 0.9, 1.0, and 2.5% lower than the accurate NHF results. We have obtained MP2 results for the argon diatom in the range $3.5 \le R/a_0 \le 12$. The results are given in Table 11 for the dipole polarizability and Table 12 for the hyperpolarizability. In Figure 4 we have plotted the mean and the anisotropies of the interaction hyperpolarizability. The analysis of the SCF and MP2 results for $\bar{\alpha}_{int}$ and $\Delta\alpha_{int}$ shows a smooth behavior. We do not observe the anomalous short-range effect noticed for the neon diatom. For the hyperpolarizability (see Figure 4) the familiar pattern is again present. It is interesting to notice the change in the order of magnitude of $\bar{\gamma}_{int}$ from $R/a_0 = 3.5$ to 12. The electron correlation effect (the D2 correction) for the interaction $\gamma_{\alpha\beta\gamma\delta}$ is comparable to the magnitude of the SCF values. This is the case for a large part of the total range of internuclear separations.

Kr···Kr. We rely on a [8s7p6d5f] basis set for our calculations. We have used again a TZV (17s13p6d)[6s5p2d] basis set.[76] The [8s7p6d5f] basis set gives for Kr the SCF values $\alpha/e^2a_0{}^2E_h{}^{-1} = 16.45$, $\alpha_2/e^2a_0{}^4E_h{}^{-1} = 95.02$ and $\gamma/e^4a_0{}^4E_h{}^{-3} = 2233$, barely 0.2, 0.6 and 1.2% below the NHF[74,78] values of 16.476, 95.55, and 2260. Thus, the starting point of our calculations is a flexible basis set of near-Hartree−Fock quality. Our study extends to the range of internuclear separations defined by $4 \le R/a_0 \le 12$. Our MP2 results are given in Tables 13 and 14 and the hyperpolarizability invariants are plotted against the internuclear separation in Figure 5. The interaction polarizability of the krypton diatom resembles closely that of argon. The evolution to large separations is very smooth. The contents of Table 14 show that interaction hyperpolarizability effects in the krypton diatom remain strong even at very large separations. At 12 a_0 the Mp2 value of $\bar{\gamma}_{int}$ is small at 1.6 $e^4a_0{}^4E_h{}^{-3}$, but the anisotropy $\Delta_1\gamma$ is of the order of magnitude of the hyperpolarizability of the krypton atom, as can be easily inferred from the $\gamma_{\alpha\beta\gamma\delta}$ components in Table 14. The magnitude

TABLE 14: Cartesian Components and Mean Value of the Interaction Second Hyperpolarizability of Two Kr Atoms[a]

	γ_{zzzz}			γ_{xxxx}			γ_{xxzz}			$\bar{\gamma}$		
R/a_0	SCF	D2	MP2	SCF	D2	MP2	SCF	D2	MP2	SCF	D2	MP2
4.0	44195.8	20528.9	64724.7	−410.7	493.3	82.3	3874.1	2185.9	6060.1	11719.3	6117.7	17837.0
4.5	13878.6	6278.7	20157.5	−1145.6	−109.9	−1255.5	634.8	446.7	1081.4	2672.5	1554.4	4227.1
5.0	6105.7	2827.9	8933.5	−1069.4	−130.6	−1200.0	−8.7	166.0	157.3	643.9	628.8	1272.5
5.5	3152.5	1514.9	4667.5	−909.8	−148.0	−1057.8	−139.5	53.5	−86.0	33.7	266.8	300.5
6.0	1843.1	963.2	2806.3	−781.7	−142.0	−923.7	−156.2	20.7	−135.5	−173.3	133.5	−39.8
7.0	974.5	564.1	1538.6	−589.9	−114.7	−704.6	−101.8	11.7	−89.9	−201.2	60.9	−140.1
8.0	816.2	431.7	1247.9	−440.9	−88.4	−529.3	−41.0	14.6	−26.4	−104.6	50.9	−53.7
9.0	731.2	325.5	1056.6	−331.9	−70.7	−402.6	−4.5	13.1	8.5	−34.4	37.7	3.4
10.0	610.0	236.6	846.5	−254.1	−51.7	−305.9	8.5	13.0	21.5	−6.7	30.2	23.5
11.0	485.8	164.2	650.0	−196.4	−44.1	−240.5	13.4	8.8	22.1	3.2	16.3	19.4
12.0	378.8	115.5	494.1	−155.1	−34.8	−190.1	13.7	5.2	18.9	3.9	8.7	12.6

[a] Analysis of MP2 results obtained with basis set [8s7p6d5f].

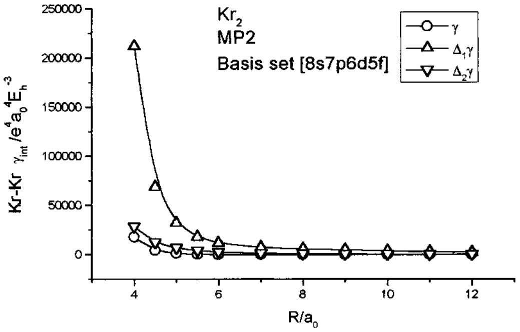

Figure 5. Interaction hyperpolarizability of two krypton atoms.

of electron correlation effects is very large, even larger than the SCF quantities in some cases.

Conclusions

We have reported an extensive investigation of the computational aspects of the interaction hyperpolarizability of $H_2\cdots H_2$, Ne⋯HF, Ne⋯FH, He⋯He, Ne⋯Ne, Ar⋯Ar, and Kr⋯Kr. There is a fair general agreement between our results and previous efforts by Papadopoulos and Waite,[19] Bishop and Dupuis,[20] Fernandez et al.,[22] Hattig et al.,[23] and Koch et al.[24] We do not proceed to a more detailed comparison, as, according to the nature of the work, this would necessitate a minute examination of the finer points of every computational effort. Such an examination would extend the discussion at inordinate length.

Summarizing the accumulated experience, we emphasize the following points:

(A) The basis sets used in the calculations should predict very accurate electric properties for the subsystems. Large, carefully optimized basis sets should always be used, especially for atoms. The optimization process should include at least the dipole polarizability of the subsystems.

(B) Interaction hyperpolarizabilities in weakly bonded molecules are small in magnitude when compared to the total property of the system or that of the subsystems. In some cases the total effect might be less than the error conventionally accepted for the monomers.

(C) Basis set effects should be studied at all levels of theory. In order to obtain conclusively valid theoretical predictions, in some cases more than one type of basis set should be used. Systematic errors associated with the initial substrate might not be removed with the enlargement of the basis set.

(D) In cases where one studies also geometry effects on the interaction properties, as seen in the study of rare gas diatoms, it is worth emphasizing that the magnitude of the effect $P_{int}(R)$ changes drastically. The very nature of the computational problem is different at short, medium, or long range.

The computational strategy defined by the aforementioned strictures and rules should help to systematize investigations in this relatively unexplored research field.

Last, as a rather significant byproduct, we have designed several basis sets that could be used in further studies on $(H_2)_n$, He_n, Ne_n, Ar_n, and Kr_n and related systems.

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