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A pseudopotential study of the hydrogen bond in $H_2O{\cdot}H_2S$, $H_2S{\cdot}H_2S$ and $H_2O{\cdot}H_2Se$ systems*

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Intermolecular potential energy curves for the hydrogen bonded systems $H_2O{\cdot}H_2S$, $H_2O{\cdot}H_2Se$ and $H_2S{\cdot}H_2S$ were calculated with nonempirical pseudopotentials using optimized-in-molecules basis sets augmented by polarization functions. The $H_2O{\cdot}H_2O$ interaction energy curve has been also considered as a test case. The present results for $H_2O{\cdot}H_2S$ and $H_2S{\cdot}H_2S$ indicate much weaker intermolecular interactions than those found in previous *ab initio* calculations. The $H_2O{\cdot}H_2Se$ interaction was found to be quite similar to $H_2O{\cdot}H_2S$.

Key words: $H_2O{\cdot}H_2S$, $H_2O{\cdot}H_2Se$, $H_2S{\cdot}H_2S$ hydrogen bonds—pseudopotential calculations—counter-poise correction

1. Introduction

It is now fairly well established that thiols can form hydrogen bonds [1]. As compared to alcohols or phenols thiols usually form relatively weak hydrogen bonds. Until about 1960 there was even doubt as to the existence of S—H···S hydrogen bonding, despite conclusive evidence for S—H···O and S—H···N [1-3]. Relatively little is known about the hydrogen bonds formed by the selenium analogues of thiols, i.e. selenols. From the similarity of the physical properties of H_2S and H_2Se, their clathrate hydrates [3, 4], as well as mercaptans and selenomercaptans [2, 3], one can expect that the SeH group can be involved in

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** On leave from Quantum Chemistry Laboratory, Dept. of Chemistry, University of Warsaw, Pasteura 1, 02-093. Warsaw, Poland hydrogen bonds similar to its —SH analog. It is interesting to note that various biochemical and biological processes do not distinguish selenium from sulfur [5, 6].

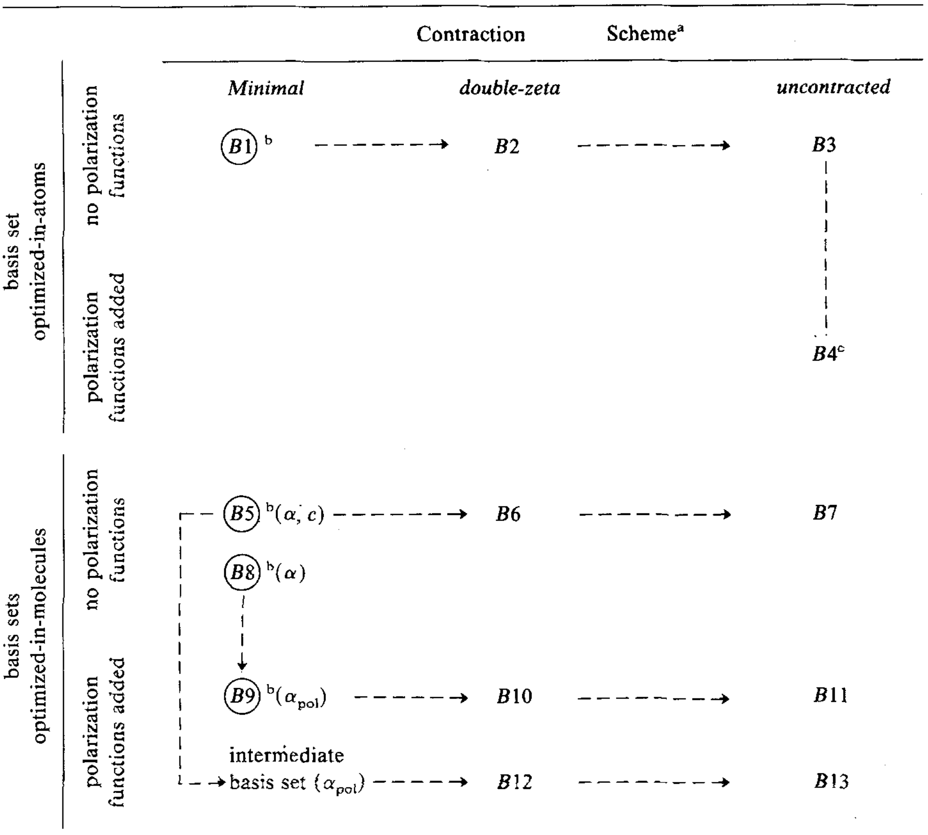
Previous *ab initio* calculations [7–10] of H···S bonding have been performed at the medium-size basis set level, primarily from consideration of computational effort. However, there remains the possibility that the interaction energies, with these limited basis sets, are overestimated. Here we consider the case of the hydrogen bonded $H_2O \cdot H_2S$ system where previous calculations with a double-zeta basis set [7] predicted an interaction energy considerably stronger than that corresponding to an $H_2O \cdot H_2O$ dimer calculated with an extended basis set [11, 12]. The relative strength of the O—H···O and S—H···O (or O—H···S) bonds is of primary importance since almost all processes involving sulfur occur in aqueous solution. This has prompted us to recalculate the interaction energy curves for the systems $H_2O \cdot H_2S$ and $H_2S \cdot H_2S$ in some more detail. For comparison we also calculated the interaction energy for the $H_2O \cdot H_2Se$ complex. The systems chosen are prototypes of the following hydrogen bonds X—H···Y, where (X, Y) = (O, S), (S, O), (S, S), (Se, O) and (O, Se), which can be present in various biochemical and biological processes. The calculations were performed within the self-consistent-field approach using nonempirical pseudopotentials [13]. We also estimated the dispersion energy contribution to the interaction.

2. Method

A nonempirical pseudopotential method [13] was used with the PSHONDO program [14]. Within this method the interaction energy between the molecules A and B has been obtained in a standard way, i.e. $\varepsilon_{\text{int}} = E_{\text{tot}}(A \cdot B) - E_{\text{tot}}(A) - E_{\text{tot}}(B)$, where the total energy of $A(B)$ corresponds to the isolated molecule. We also considered counterpoise (CP) correction for basis set superposition error [15], where the total energy of $A(B)$ was calculated in the basis set of a dimer.

Several gaussian basis sets, denoted $B1$ to $B13$, have been used in the present work. In all cases the s and p atomic orbitals consisted of four primitive gaussians. Our bases can be classified with respect to the contraction scheme and the optimization procedure, see Table 1. The contraction scheme involves "minimal" (one function per symmetry), "double zeta" (two functions per symmetry) and "uncontracted" (four functions per symmetry). Within each of these schemes polarization functions can be added: one d function on heavy atom and one p on hydrogen atom. The construction of molecular basis set involves two optimization procedures. In the first one, the basis set was optimized in atoms (in their ground state) by means of the PSATOM program [16]. In the second, we varied the exponents (and, in some cases, the contraction coefficients) of the former basis in order to lower the total energy of the molecule. This was done with the inclusion of a quasi Newton algorithm applied to the PSHONDO program. The details of further investigations concerning optimized-in-molecules basis sets for pseudopotential calculations will be given elsewhere [18].

Table 1. The notation of the molecular basis sets



		Contraction Scheme[a]		
		Minimal	*double-zeta*	*uncontracted*
basis set optimized-in-atoms	no polarization functions	ⓑ*B1*[b] →	*B2* →	*B3*
	polarization functions added			*B4*[c]
basis sets optimized-in-molecules	no polarization functions	*B5*[b]$(\alpha; c)$ → *B8*[b](α)	*B6* →	*B7*
	polarization functions added	*B9*[b](α_{pol}) → intermediate basis set (α_{pol}) →	*B10* → *B12* →	*B11* *B13*

[a] Minimal $(4, 4/4) \rightarrow [1, 1/1]$; double-zeta $(4, 4/4) \rightarrow [2, 2/2]$ in groups $\{3, 1\}$.

[b] Circles mean the optimization of the basis set; in parentheses are the varied parameters: α-the exponents of s and p functions, c-the contraction coefficients and α_{pol}-the exponents of polarization functions; the horizontal dotted arrows mean the decontraction while the vertical ones - the expansion of the basis set by polarization function.

[c] In H_2O two $d(\alpha = 1.5, 0.4)$ functions on oxygen and one $p(\alpha = 0.75)$ function on hydrogen were added

The calculated interaction energies were corrected by the dispersion energy term, estimated by means of a London-type formula $\varepsilon_{disp} = -C_6R^{-6}$ [22]; where C_6 coefficient is related to the ionization potentials and the polarizabilities of interacting species.

All calculations were performed for experimental geometries: $d(OH) = 0.957$ Å, $\measuredangle HOH = 104.52°$ for H_2O, and $d(SH) = 1.328$ Å, $\measuredangle HSH = 92.20°$ for H_2S [23] and $d(SeH) = 1.460$ Å, $\measuredangle HSeH = 91.20°$ for H_2Se molecule [23].

3. Results

In order to assess the quality of the different basis sets we compared molecular properties which are mostly dependent on the valence electrons: the valence orbital energies, total energy differences and the dipole moments of H_2O and H_2S. In Tables 2 and 3 we present the respective values obtained for the basis sets with or without polarization functions. For comparison we also added the results of all electron near-limit Hartree-Fock calculations. One can see that the "minimal" optimized-in-atoms basis set, *B*1, behaves less satisfactory than the "minimal" optimized-in-molecules basis sets *B*5 and *B*8. The difference between the last two bases is in the number of variational parameters involved in the optimization process. In one case, *B*8, only the exponents were varied whereas in the second case, *B*5, both exponents and contraction coefficients were optimized. However, as one can see from Tables 2 and 3, these basis sets are equivalent. Probably the most interesting result is that one can attain results of similar quality to the "double-zeta" (*B*2) with the "minimal" optimized-in-molecules basis sets (*B*5 or *B*8). One can also observe that the values of orbital energies and of dipole moment obtained with basis sets which do not include polarization functions are

Table 2. Total energy differences[a], valence orbital energies and dipole moment of H_2O molecule in various basis sets. Energies in a.u., dipole moment in Debyes

			$-\varepsilon$				
Basis	Contraction	Δ^a	$2a_1$	$3a_1$	$1b_1$	$1b_2$	μ
no polarization functions in the basis set							
*B*1	[1, 1/1]	0.084	1.339	0.549	0.503	0.609	2.31
*B*8	[1, 1/1]	0.062	1.360	0.564	0.512	0.706	2.48
*B*5	[1, 1/1]	0.048	1.362	0.562	0.506	0.708	2.86
*B*2	[2, 2/2]	0.044	1.359	0.559	0.501	0.710	2.61
*B*6	[2, 2/2]	0.037	1.369	0.567	0.507	0.720	2.74
*B*3	[4, 4/4]	0.038	1.359	0.559	0.501	0.710	2.62
*B*7	[4, 4/4]	0.034	1.368	0.568	0.507	0.719	2.70
polarization functions in the basis set							
*B*9	[1, 1, 1/1, 1]	0.018	1.342	0.572	0.505	0.702	2.07
*B*12	[2, 2, 1/2, 1]	0.002	1.352	0.576	0.505	0.713	2.22
*B*4	[4, 4, 2/4, 1]	0.000	1.340	0.569	0.497	0.704	1.99
*B*13	[4, 4, 1/4, 1]	reference	1.353	0.578	0.506	0.714	2.21
best SCF *ab initio*			1.351	0.584	0.508	0.717	2.08[b] (2.21)[c]

[a] The differences of the total energies, Δ, are defined with respect to the reference total energy calculated in the *B*13 basis set.

[b] Near limit Hartree-Fock calculations [24]; $E_{tot} = -76.062$ a.u. in the basis set (11, 7, 2/5, 1) contracted to [6, 5, 2/3, 1]. The best Hartree-Fock calculations [25] predict $E_{tot} = -76.066$ a.u., however, the corresponding orbital energies and dipole moment were not available.

[c] Near limit Hartree-Fock calculations [25]; $E_{tot} = -76.060$ a.u. in the uncontracted basis set (12, 7, 1/7, 1); for comparison the experimental dipole moment is $\mu_{exp} = 1.85$ D [26]

Table 3. Total energy differences[a], valence orbital energies and dipole of H_2S molecule in various basis sets. Energies in a.u., dipole moment in Debyes

Basis	Contraction	Δ[a]	$-\varepsilon$				μ
			$4a_1$	$5a_1$	$2b_1$	$2b_2$	
no polarization functions in the basis set							
*B*1	[1, 1/1]	0.079	1.016	0.497	0.404	0.600	2.17
*B*8	[1, 1/1]	0.065	1.004	0.486	0.389	0.591	2.35
*B*5	[1, 1/1]	0.064	1.003	0.486	0.389	0.592	2.37
*B*2	[2, 2/2]	0.054	1.008	0.490	0.389	0.595	1.95
*B*6	[2, 2/2]	0.052	1.004	0.489	0.385	0.594	2.27
*B*3	[4, 4/4]	0.048	1.005	0.491	0.388	0.595	1.90
*B*7	[4, 4/4]	0.050	1.006	0.491	0.387	0.595	2.12
polarization functions in the basis set (cf. Table 2)							
*B*9	[1, 1, 1/1, 1]	0.012	0.978	0.489	0.377	0.585	1.89
*B*10	[2, 2, 1/2, 1]	0.002	0.985	0.497	0.379	0.592	1.65
*B*11	[4, 4, 1/4, 1]	reference	0.986	0.499	0.381	0.594	1.51
best SCF			0.982[b]	0.500	0.382	0.592	1.28
ab initio			0.980[c]	0.494	0.379	0.588	—
			0.979[d]	0.495	0.380	0.588	—

[a] The differences of the total energies, Δ, are defined with respect to the reference total energy calculated in the *B*11 basis set.

[b] Near limit Hartree-Fock calculations [27]; $E_{tot} = -398.682$ a.u.

[c] Near limit Hartree-Fock calculations [28]; basis set (11, 7, 1/5, 1) [contracted to 7, 4, 1/3, 1].

[d] Near limit Hartree-Fock calculations [28]; basis set (11, 7, 2, 1/5, 1) contracted to [7, 4, 2, 1/5, 1]; for comparison the experimental dipole moment $\mu_{exp} = 0.97$ D [26]

Table 4. The SCF interaction energy (kcal/mole) in $H_2O{\cdot}H_2O$ system, see Fig. 1

R_{oo} (a.u.)	All electron[a]	Pseudopotential[b]	
Basis set	Extended	*B*9[c]	*B*12[c]
4.0	34.62	— (43.90)[d]	—
4.4	10.72	14.69 (13.73)	10.26 (9.43)
4.8	0.92	— (1.74)	0.30 (−0.38)
5.2	−2.77	— (−2.56)	−3.40 (−3.96)
5.67	−3.87	−3.55 (−3.87)	−4.50 (−4.93)
7.0	−2.69	−2.59 (−2.65)	−3.05 (−3.19)
9.0	−1.14	— (−1.11)	—
15.0	−0.21	— (−0.21)	

[a] Ref. [12].

[b] Present work.

[c] See Table 2.

[d] In parentheses the values obtained in a standard way i.e. not counter-poise corrected

Table 5. The SCF interaction energy (kcal/mole) in $H_2O{\cdot}H_2S$ system in the geometry *B*, See Fig. 2

R_{so} (a.u)	Basis set	All electron 4G[a]	4-31G[a]	Double zeta[b]	Pseudopotential *B*2[c]	*B*10 and *B*12[c]
5.5		—	—	—	—	+7.37 (+6.53)[d]
6.0		−0.01	−2.70	+14.2	−2.38 (−3.39)	+0.63 (−0.01)
6.4		−0.94	−3.57	−5.10	—	—
6.5		—	−3.62	−5.10	−3.41 (−4.07)	−1.70 (−2.19)
6.6		—	−3.64	−5.09	—	—
6.8		−1.07	−3.59	−4.98	—	—
7.0		—	—	—	−3.21 (−3.72)	−2.24 (−2.58)
7.2		−0.94	—	—	—	—
7.5		—	—	—	—	−2.12 (−2.36)
7.6		−0.76	—	—	—	—

[a] Ref. [30].
[b] Ref. [7].
[c] See Tables 2 and 3.
[d] In parentheses the values obtained in a standard way, i.e. not counter-poise corrected

rather far from the best all electron calculations. On the contrary, when polarization functions are included, the agreement with the best *ab initio* results is remarkably better. Comparing the data presented in Tables 2 and 3 it seems clear that "double-zeta+polarization" bases *B*10 and *B*12 yield results of similar quality as extended calculations for isolated molecules. These basis sets have

Table 6. The SCF interaction energy (kcal/mol) in $H_2O{\cdot}H_2S$ system in the geometry *A*, see Fig. 3

R_{so} (a.u.)	Basis	All electron 4G[a]	4-31G[a]	Double zeta[b]	Pseudopotential *B*10 and *B*12[c]
6.0		—	—	+0.55	+2.66 (+2.15)[d]
6.4		−1.36	−1.92	−1.19	—
6.5		−1.39	—	—	+0.13 (−0.23)
6.6		−1.40	—	—	—
6.8		−1.34	−2.37	−1.81	
7.0		—	−2.38	—	−0.76 (−1.01)
7.2		—		−2.08	—
7.5		—	—		−0.99 (−1.14)
7.6		—		−1.92	—
8.0		—	—	—	−0.96 (−1.05)
8.5		—	—	—	−0.68 (−0.73)

[a] Ref. [30].
[b] Ref. [7].
[c] See Tables 2 and 3.
[d] In parentheses the values obtained in a standard way, i.e. not counter-poise corrected

Table 7. The SCF interaction energy (kcal/mole) in $H_2S{\cdot}H_2S$ system, see Fig. 4

R_{ss} (a.u.)	*ab initio*	Pseudopotential[a]
6.0	—	+18.76 (+17.90)[b]
7.0	—	+2.68 (+2.14)
7.9	−1.4[c]	—
8.0	−0.9[d]	−0.31 (−0.62)
8.1	−1.5[c]	—
8.2	−1.0[d]	—
8.3	−1.8[e]	—
8.5	−0.7[f]	−0.58 (−0.81)
9.0	—	−0.62 (−0.78)
9.5	—	−0.58 (−0.68)

[a] Basis *B*10, see Table 3.

[b] In parentheses the values obtained in the standard way, i.e. not counter-poise corrected.

[c] Ref. [8], basis I optimized for atoms; ε_{int} not counter-poise corrected.

[d] Ref. [8], basis II partly optimized for H_2S molecule; ε_{int} not counter-poise corrected.

[e] Ref. [10], basis 4-31G.

[f] Ref. [9], basis (12, 9/3) contracted to (minimal) [3, 2/1]; ε_{int} not counter-poise corrected

been applied to the computations of interaction energy curves for $H_2O{\cdot}H_2O$, $H_2O{\cdot}H_2S$, $H_2O{\cdot}H_2Se$ and $H_2S{\cdot}H_2S$ complexes. Within pseudopotential approach the systems chosen are isoelectronic and require the same computational effort. The results are presented in Tables 4-8 and Figs. 1-6.

The $H_2O{\cdot}H_2O$ system was chosen as a test case for our basis sets. From Table 4 and Fig. 1 one can see that the interaction energy obtained at the "double-zeta+polarization" level (*B*12) is close to the one of the best all electron calculations on this system [12]. The discrepancy of about 0.6 kcal/mole at minimum can probably be ascribed to the slightly different dipole moments (2.06D [12] and

Table 8. The SCF interaction energy (kcal/mole) in $H_2O{\cdot}H_2Se$ system

R_{O-Se} (a.u)	geometry *B*[a]	*A*[b]
6.0	4.61 (3.68)[c]	5.74 (5.05)
7.0	−1.39 (−1.88)	0.45 (0.08)
8.0	−1.65 (−1.86)	−0.36 (−0.54)
9.0	−1.18 (−1.27)	−0.38 (−0.49)

[a] See Fig. 2.

[b] See Fig. 3.

[c] In parentheses the values not counter-poise corrected

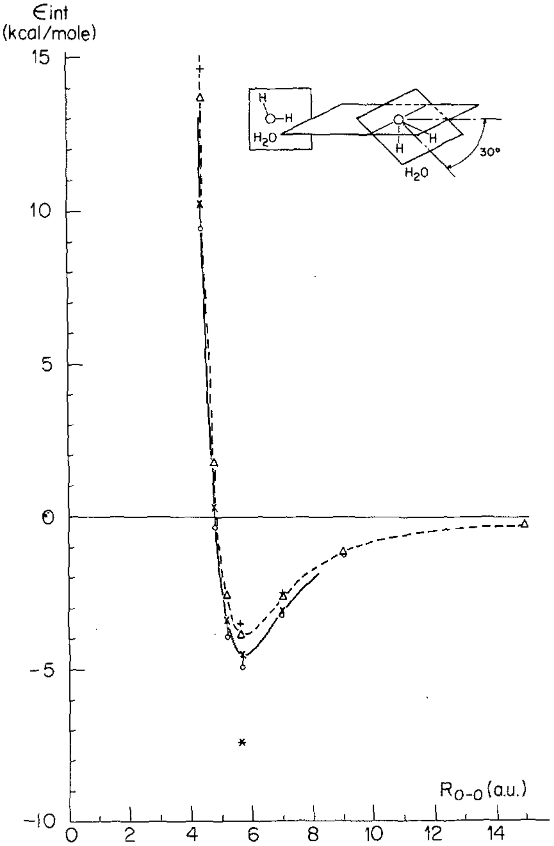


Fig. 1. The $H_2O{\cdot}H_2O$ interaction energy curve; dotted line *ab initio* near limit Hartree-Fock calculations [12]; full line-present work; ○○○ and × × × × standard and counterpoise corrected ε_{int}, respectively, (basis *B*12); △△△△ and + + + + standard and counterpoise corrected ε_{int}, respectively, (basis *B*9);* standard ε_{int}, (basis *B*5)

2.22D present). For comparison, we have also calculated the interaction energy curve with a smaller basis set (*B*9) obtaining even better agreement with all electron cases. Of course, the numerical agreement is a coincidence, however, the closeness of this basis set predictions to those of the "double-zeta+polarization" basis set is quite regular, as will be shown afterwards. Nevertheless, one has to mention that in previous all electron calculations of the interaction energy the "minimal+polarization" basis set was found to be quite poor [33]. We can try to see if an even smaller basis set than *B*9, i.e. *B*5, which does not include polarization function can be used. However, we obtained at minimum $\varepsilon_{\text{int}} = -7.34$ kcal/mole which is almost 100% in excess of the respective all electron value. This had led us to the conclusion that in pseudopotential calculations similar to the all electron case [29] polarization functions in the basis set are necessary to obtain reliable values of the interaction energy.

Once we have established the necessary level for attaining reasonable results we decided to consider two hydrogen-bonded situations for $H_2O{\cdot}H_2S$ systems. The first corresponds to the structure *B* of the work of del Conde and Novaro [7] where the water molecule acts as a proton acceptor. For the second, denoted in

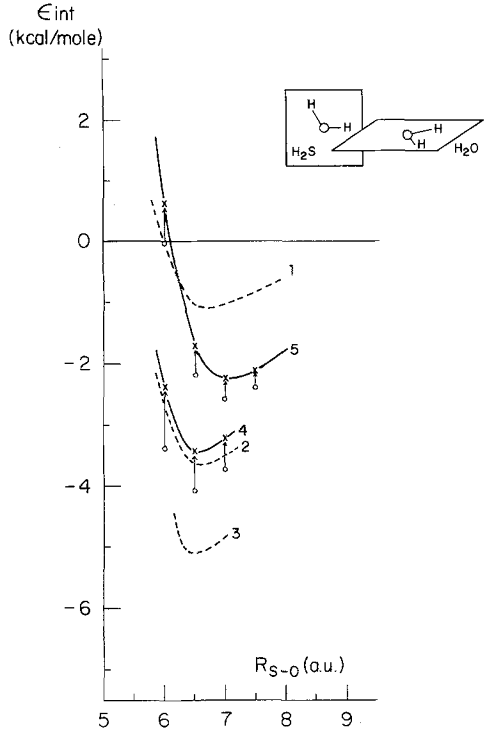


Fig. 2. The $H_2O{\cdot}H_2S$ interaction energy curve in geometry *B* [7]; dotted lines-*ab initio*, full lines-pseudopotential; (1) 4G basis set [30]; (2) 4-31G basis set [30]; (3) double zeta basis set [7]; (4) basis *B*2. (OOOO and × × × × standard and counterpoise corrected ε_{int}, respectively); (5) basis *B*12 for H_2O and *B*10 for H_2S (OOOO and × × × × standard and counterpoise corrected ε_{int}, respectively)

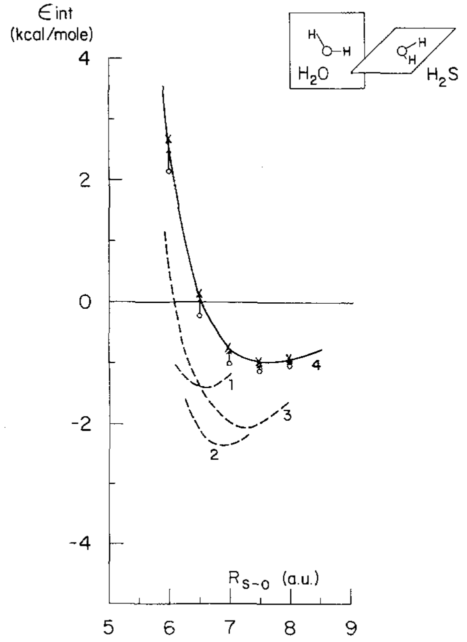


Fig. 3. The $H_2O{\cdot}H_2S$ interaction energy curve in geometry A [7]; dotted lines-*ab initio*, full line-pseudopotential; (1) 4G basis set [30]; (2) 4-31G basis set [30]; (3) double zeta basis set [7]; (4) basis *B*12 for H_2O and *B*10 for H_2S (OOOO- and × × × ×- standard and counterpoise corrected ε_{int}, respectively)

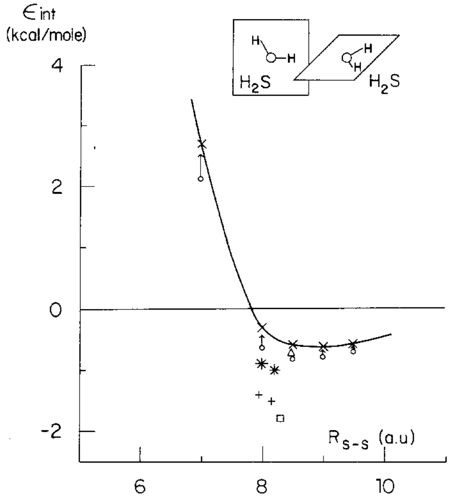


Fig. 4. The $H_2S{\cdot}H_2S$ interaction energy curve; basis $B10$ (○○○○ and × × × × standard and counterpoise corrected ε_{int}, respectively); Δ Ref. [9]; ** optimized-in-molecules basis set [8]; + + basis set optimized for atoms [8]; □ 4-31G basis set [10]

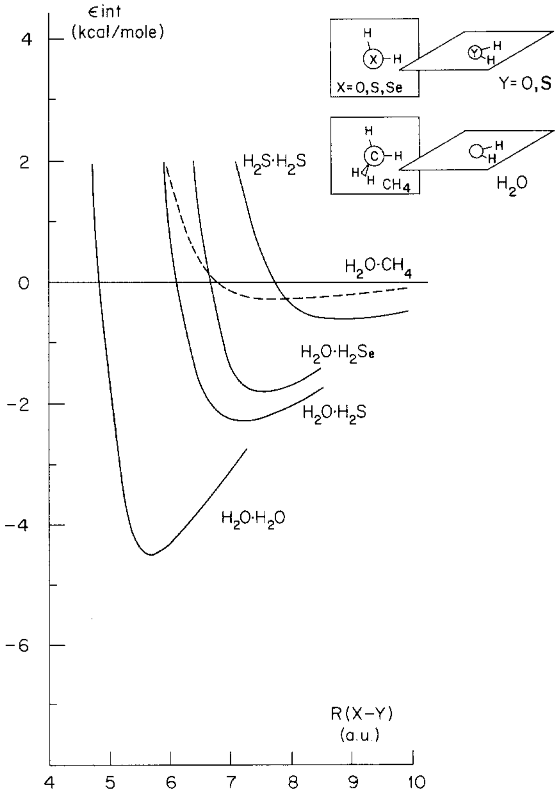


Fig. 5. The SCF pseudopotential interaction energies in $H_2O{\cdot}H_2X$; X = O, S, Se, complexes in hydrogen bonded geometry where water molecule acts as a proton acceptor. The dotted line represents the *ab initio* [31] curve for $H_2O{\cdot}CH_4$ interaction in analogous geometry. For comparison pseudopotential $H_2S{\cdot}H_2S$ interaction energy curve added

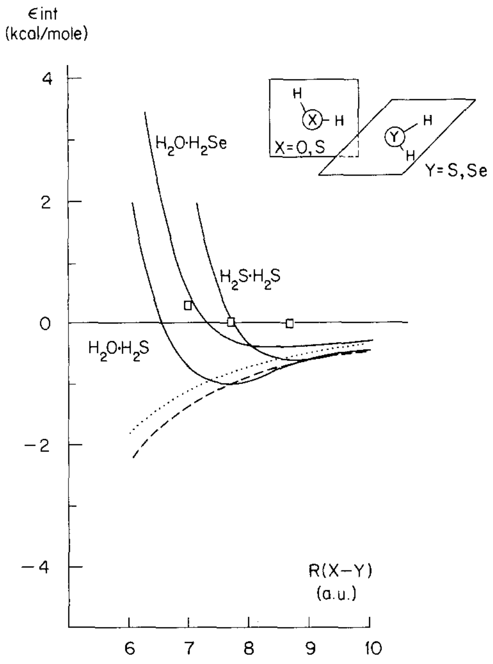


Fig. 6. The SCF pseudopotential interaction energies in $H_2X{\cdot}H_2O$, X = S, Se, complexes in hydrogen bonded geometry where water molecule acts as a proton donor. - - - and · · · curves represent a "classical" dipole–dipole and dipole–induced dipole interactions in $H_2S{\cdot}H_2O$ and $H_2Se{\cdot}H_2O$ systems, respectively. □□□ the *ab initio* interaction energy for $Ar{\cdot}H_2O$ [32]. For comparison pseudopotential $H_2S{\cdot}H_2S$ interaction energy curve added

the quoted paper as *A*, the same role is played by H_2S. The calculated interaction energies for *B* and *A* structures are presented in Tables 5 and 6 and Figs. 2 and 3, respectively. For comparison we consider the results of the best available *ab initio* calculations for this system [7] which were performed with a double-zeta basis sets without polarization functions. We also consider the results of all electron calculations with smaller basis sets i.e. minimal and 4-31G [30]. For the structure *B*, we also present pseudopotential calculations with a "double-zeta" type basis set, *B*2. One can see that our interaction energy curves, obtained with the optimized-in-molecules basis sets augmented by polarization functions considerably differ from the all electron double-zeta calculations. We found that with respect to these results, for both geometries at the minimum, the water molecule interacts with the hydrogen sulfide molecule considerably weaker and at longer intermolecular distances. If we compare *A* and *B* structures we can confirm the former conclusion [7] that there is an asymmetric behaviour when the proton donor molecule of the hydrogen bonded pair is changed to proton acceptor.

We also locked to the charge transfer in both structures, however, no detectable transfer (below 0.001 a.u.) were found at minimum in contradiction to the results of the former all electron calculation [7]. The electron acceptor nature of H_2S in geometry *B* was slightly established at shorter intermolecular distances: the net charge of H_2S molecule was found to be: −0.027, −0.008, −0.002 and 0.000 a.u. at $R_{so} = 5.5$, 6.0, 6.5 and 7.0 a.u., respectively.

For the $H_2S\cdot H_2S$ system we only consider one hydrogen-bonded situation, which is depicted on Fig. 4. The numerical values of the interaction energy are presented in Table 7. Similarly to the former case our results for the interaction energy differ from the available all electron computations [8–10] and predict at the minimum a very weak interaction comparable to the energy of the thermal motions at room temperatures. Here we would like to mention the rather clear influence of the basis set on the calculated interaction energy, similar to the $H_2O\cdot H_2S$ case. The results of those all electron calculations which do include polarization functions in the basis set [8] agree well with our interaction energy curve and, on the contrary, the calculations with 4-31G basis set [10] are far from it. The results of Sabin's calculations [9] in the minimal basis suffer probably from significant superposition basis error [29, 38] and, consequently, after counterpoise correction the interaction energy curve should become considerably more repulsive.

For the $H_2O\cdot H_2Se$ system we considered the same hydrogen bonded geometries as for $H_2O\cdot H_2S$. We used "double zeta+polarization" basis sets, $B12$ and $B10$, for H_2O and H_2Se molecules, respectively. The calculated interaction energies are present in Table 8 and Figs. 5 and 6.

We also wanted to study the effect of basis set superposition error [15]. This error was found to be, at minima for all cases, of the order of 0.2–0.4 kcal/mole. Although its absolute value is rather small it reduces the $H_2O\cdot H_2O$, $H_2O\cdot H_2S$, $H_2O\cdot H_2S$ interaction energies by 9, 13, 11 and 20%, respectively. Thus all our calculations were corrected by means of counterpoise method [15].

In the present work we have also estimated the dispersion energy contribution to the interaction energy by means of London-type formula [22]. We used the available values of $C_6(H_2O\cdot H_2O) = 45.37$ a.u. [34, 35], $\alpha(H_2S) = 25.5$ a.u. [36], $\alpha(H_2Se) = 32.2$ a.u. [36], $I(H_2S) = 10.44$ eV [37], $I(H_2Se) = 9.5$ eV (equal to the highest occupied orbital energy in the present calculations) and a combination rules for dispersion energy coefficients [35]. We obtained the following values of C_6: $C_6(H_2O\cdot H_2S) = 89.0$ a.u., $C_6(H_2O\cdot H_2Se) = 106$ a.u. and $C_6(H_2S\cdot H_2S) = 187$ a.u. It is known [38] that London-type formulas underestimate the values of dispersion energy approximately by a factor of two, as in the case of $H_2O\cdot H_2O$ interaction [12]. Therefore, in order to have a most realistic estimation of dispersion energy we multiplied the C_6 coefficient by a factor of two and used it in the London-type formula. The consequent changes for the parameters of the minima after dispersion energy correction are presented in Table 9. One can observe that our results for the equilibrium distances are consistent with estimates based on Van der Waals radii [39, 40] as well as with recent all electron extended basis set calculations on the $O\cdots HS$ bond [48].

4. Discussion

In the present work we have shown the ability of optimized-in-molecules basis sets to predict both the properties of isolated molecules and their interaction energies. We stressed that polarization functions in the basis set are necessary to

Table 9. The parameters of minima of the interaction energy curves for $H_2O{\cdot}H_2S$, $H_2S{\cdot}H_2S$ and $H_2O{\cdot}H_2Se$ systems

	SCF		SCF+dispersion		Maximum[a] R(X···Y) for H bond (Å)	R(X···Y)[a] sum of contact radii (Å)	Type of H bond X—H···Y
	ε (kcal/mole)	r_{min} (Å)	ε (kcal/mole)	r_{min} (Å)			
$H_2O{\cdot}H_2S$ (config. B)	−2.2	3.7	−3.3	3.6	3.7	3.9	S—H···O
	−1.5[b]	3.8[b]	−3.0[b]	3.5[b]			
$H_2O{\cdot}H_2S$ (config. A)	−1.0	4.1	−1.7	3.8	3.8	4.0	O—H···S
$H_2S{\cdot}H_2S$	−0.6	4.7	−1.3	4.3	4.2	4.4	S—H···S
$H_2O{\cdot}H_2Se$ (config. B)	−1.7	4.2	−2.5	3.7	3.9	4.1	Se—H···O
$H_2O{\cdot}H_2Se$ (config. A)	−0.4	4.8	−0.9	4.2	4.0	4.2	O—H···Se

[a] See Ref. [39, 40].

[b] The results of all electron extended basis set calculations on the $H_2CO{\cdots}H_2S$ system (config. I) [48].

obtain reasonable agreement with extended calculations. Similar conclusions have been repeatedly pointed out since the early 1960's with respect to the all electron calculations with small basis sets [29]. However, within the pseudopotential approach, polarization functions augmenting the original basis sets, have been used surprisingly seldom (see for example [41, 45]). We have also shown that molecular optimization of the basis sets, especially the small ones, seems to be a good tool to obtain reasonable results. Similar investigations, although limited to a partial optimization of the basis sets, in all electron calculations have been performed for a long time [21, 42, 44].

In the present work we have used the experimental geometry of H_2O,H_2S and H_2Se molecules. It is known [21] that geometries of the molecules containing first- or second-row atoms optimized in small basis sets slightly differ from the experimental values: bond lengths are generally overestimated by 0.03-0.05 Å while bond angles are reproduced with accuracy of about two degrees. The relaxation of intramolecular geometry in extended basis sets leads to even less marked changes which have a minor influence on the calculated interaction energies [25, 49]. This relaxation, however, can have a remarkable effect on the dipole moment derivatives for the molecules being proton donors in hydrogen bonded systems [43]. Those derivatives are directly related to the infrared spectra. The observed increase of infrared intensity of AH stretching mode on AH···B hydrogen bond formation is proportional to the square of the corresponding dipole moment derivatives:

$$I_R = \frac{|\partial\mu/\partial d|^2_{\mathrm{AH\cdots B}}}{|\partial\mu/\partial d|^2_{\mathrm{AH}}} \tag{1}$$

where d is the length of the AH bond. In the present work we performed some exploratory calculations of the I_R quantity at the "minimal+polarization" basis set level ($B9$). Firstly, we optimized the geometry of H_2O, H_2S and H_2Se obtaining: $d(\mathrm{OH}) = 1.829$ a.u., $\measuredangle 105.35°$, $d(\mathrm{SH}) = 2.509$ a.u., $\measuredangle 94.86°$ and $d(\mathrm{SeH}) = 2.794$ a.u., $\measuredangle 94.30°$, respectively. Then we varied the AH bond length in these molecules, as well as in the hydrogen bonded systems, in order to calculate the respective dipole moment derivatives. We also determined the energy minima when this relaxation was included. The results are presented in Table 10. For comparison the results of all electron calculations [49] for $(H_2O)_2$ were also added. One can see that for water dimer we obtained a reasonable value of I_R, (10.6), which is in better agreement with the experimental result of $I_R = 12$ [43] than the value of $I_R = 5.3$ found in all electron calculations [49]. For water dimer we also performed the calculations with "double-zeta+polarization" basis set ($B12$). In spite of the more extended basis set the value of I_R, (18.8), is in poorer agreement with both experiment and all electron result. This should not be surprising because the I_R quantity is a very sensitive function of the basis set, similar to the dipole moment (see Tables 2 and 3) or to the dipole moment derivatives (see Table 10). Even if the actual values are crude estimates we can expect that the relative behaviour of I_R calculated at the same basis set level and in a similar system is reliable. For $H_2O \cdot H_2S$ and $H_2O \cdot H_2Se$ complexes we obtained

Table 10. Dipole moment derivatives of the proton donor molecules

Hydrogen bond	R_{AB} a.u.	Δd (AH) a.u.	$\lvert\partial\mu/\partial d\rvert_{AH\cdots B}$ a.u.	$\lvert\partial\mu/\partial d\rvert_{AH}$ a.u.	I_R a.u.
$H_2O{\cdot}H_2O$	5.67	0.007	0.65	0.20	10.6
		0.011^a	0.49^a	0.11^a	18.8^a
		0.007_5^b	0.45^b	0.19^b	5.3^b
$H_2O{\cdot}H_2S$ [c]	7.00	0.017	0.44	0.22	4.0
$H_2O{\cdot}H_2Se$ [c]	8.00	0.005	0.28	0.14	4.0

[a] Present work, *B*12 basis set.

[b] All electron extended basis set calculation [49].

[c] Geometry *B*, see Fig. 2

$I_R = 4.0$ which suggests that infrared intensities of the AH stretching modes should be about 2.5 times smaller than in water dimer. The interaction energies of $(H_2O)_2$, $H_2O{\cdot}H_2S$ and $H_2O{\cdot}H_2Se$ pairs (in *B*9 bases) of −3.9, −2.4 and −1.7 kcal/mole, respectively, were found to be slightly affected by the AH bond length variation (0.02 − 0.04 kcal/mole). As can be seen from Tables 4, 5 and 8 those interaction energies are quite reasonable estimates of our "double-zeta+polarization" calculations.

A detailed study of the behaviour of the basis sets used here will be presented elsewhere [18]. However here we present a general panorama. In the case of H_2O and H_2S we studied the dependence of valence orbital energies and dipole moment on the basis set. With the bases contracted to [2, 2, 1/2, 1] one can obtain results very close to the limit, which is estimated by means of our uncontracted basis sets. The pseudopotential limit values of orbital energies and dipole moments, are in reasonable agreement with the best all electron Hartree-Fock calculations. This suggests that the core-valence electron coupling does not affect these properties. Our results also suggest that the pseudopotentials obtained for isolated atoms can be directly transferred into molecules, i.e. there is probably no need for elaboration of "molecular" pseudopotentials. Nevertheless it has been pointed out [45] that a molecular bonding accompanied by strong charge transfer can modify the "atomic" pseudopotential. To clarify both points it would be desirable to perform analogous pseudopotential calculations with larger basis sets and for a variety of molecular properties.

Our results for the interaction energies can be affected by the basis set extension, particularly for the systems involving H_2S and H_2Se. It is rather commonly accepted that dipole moments can be useful as a guide to predict the behaviour of the interaction energy of polar molecular in hydrogen bonded systems. Thus, from the values of $\mu^{H_2S} = 1.65D$ (*B*10 basis) and $\mu^{H_2S} = 1.28D$ (all electron, extended basis set calculations [27]) we can expect that our values for the interaction energies in $H_2O{\cdot}H_2S$ and $H_2S{\cdot}H_2S$ systems are likely to be overestimated. Fortunately, at minimum the correction for the dipole-dipole interaction (when $\mu = 1.65D$ is substituted by $\mu = 1.28D$) is quite small, not exceeding 0.2-0.3 kcal/mole, which amounts to the value of the basis set superposition error.

In Fig. 5 we compare our best, i.e. "double-zeta+polarization", SCF interaction energies for $H_2O{\cdot}H_2X$, X = O, S, Se, systems in the hydrogen bonded geometry where water molecule acts as a proton acceptor. We can see a similarity of $H_2O{\cdot}H_2S$ and $H_2O{\cdot}H_2Se$ interactions which are considerably weaker than those in the analogous $H_2O{\cdot}H_2O$ dimer. Moreover one can realize that the $H_2O{\cdot}H_2S$ and $H_2O{\cdot}H_2Se$ interactions are intermediate between the "hydrophobic" [46], as in $H_2O{\cdot}CH_4$ system [31], and the water hydrogen bond interactions. A similar pattern can be found for an alternative hydrogen bonded geometry where water molecule acts as a proton donor. As we can see on Fig. 6 the $H_2O{\cdot}H_2S$ and $H_2O{\cdot}H_2Se$ interactions are even closer to another "hydrophobic" interaction, as in the $H_2O{\cdot}Ar$ system [32], except for a weak attraction which mainly results from ("classical") dipole-dipole and dipole-induced dipole interaction.

In the present work we estimated the dispersion energy contribution to the interactions calculated at the SCF level. For systems containing sulphur and selenium this contribution amounts to 40-50%. One can therefore expect considerably less directionality of hydrogen bonds in $H_2O{\cdot}H_2S$ $H_2O{\cdot}H_2Se$ and $H_2S{\cdot}H_2S$ systems. This last conclusion can be supported by the recent *ab initio* SCF calculations in the 4-31G basis set [30] where a small barrier for rotation of H_2S molecule in hydrogen bonded $H_2O{\cdot}H_2S$ dimer was found.

From the comparison of the estimated parameters of minima for various hydrogen bonded systems several observations can be made: X—H···O and O—H···X, X = S, Se, hydrogen bonds are considerably different, the former being almost twice as more attractive; X—H···O, X = S, Se, hydrogen bond strength represents roughly half of that of the water hydrogen bond; O—H···, X = S, Se, and S—H···S hydrogen bond is similar to the interaction of water with hydrophobic species. The strength of this "bond" or better say "interaction" [46] belongs to the interval of 1.0 ÷ 1.5 kcal/mole. Together with putative lack of directionality one can expect that this type of "bond" is unlikely to be present when room

Table A1. The pseudopotential parameters for O, S and Se atoms

$$W_l = \exp(-\alpha r^2) \sum_k C_k r^{n_k}, \qquad l = 0, 1, 2$$

Atom	l	α	C_1	n_1	C_2	n_2	C_3	n_3
O[a]	0	10.373 870	1.647 681	−1	45.078 280	0	—	—
	1	25.320 090	−7.790 734	0	—	—	—	—
S[a]	0	2.341 491	0.143 746	−2	27.451 005	0	−15.832 530	2
	1	2.653 882	4.302 655	−1	7.619 814	0	0.845 051	2
	2	1.136 490	−0.743 090	−1	—	—	—	—
Se[b]	0	0.673 650	3.760 650	−2	−0.355 660	2	—	—
	1	0.701 840	3.256 580	−2	−0.179 210	2	—	—
	2	0.482 210	1.223 630	−2	0.062 250	2	—	—

[a] Refs. [16, 41].

[b] Ref. [13]

Table A2. The "double-zeta+polarization" basis sets optimized in pseudopotential calculations for H_2O, H_2S and H_2Se molecules

	H_2O		H_2S		H_2Se	
	Exponents	Contraction coefficients	Exponents	Contraction coefficients	Exponents	Contraction coefficients
Heavy atom						
s	5.779 268	−0.139 478	4.360 423	0.085 282	4.960 686	−0.022 128
s	1.272 318	0.283 079	1.983 196	−0.370 820	1.556 162	−0.232 561
s	0.559 623	0.534 163	0.428 706	0.650 682	0.306 772	0.746 159
s	0.247 498	1.000 000	0.152 791	1.000 000	0.131 642	1.000 000
p	12.662 193	0.063 529	1.832 185	−0.110 945	3.478 423	−0.032 201
p	2.971 050	0.256 392	1.098 696	0.212 329	0.440 778	0.414 745
p	0.829 612	0.505 112	0.376 505	0.561 775	0.175 644	0.506 592
p	0.214 450	1.000 000	0.113 822	1.000 000	0.053 933	1.000 000
d	0.715 847	1.000 000	0.701 475	1.000 000	0.362 163	1.000 000
Hydrogen						
s	8.020 733	0.084 153	8.022 267	0.056 752	8.021 475	0.056 752
s	1.480 731	0.335 516	1.453 396	0.260 141	1.447 115	0.260 141
s	0.671 579	0.546 603	0.466 638	0.532 846	0.424 867	0.532 846
s	0.179 534	1.000 000	0.265 998	1.000 000	0.249 733	1.000 000
p	0.856 698	1.000 000	0.684 937	1.000 000	0.737 549	1.000 000

Contraction coefficients are not normalized

temperatures are considered. This, however, does not exclude the possibility that at low temperatures such an interaction can be detected by spectroscopical measurements, as in the case of hydrogen sulfide placed on the solid nitrogen matrices [1, 47].

5. Appendix

In the present pseudopotential approach the hamiltonian contains the atomic pseudopotential operator given by the form $W_{ps} = -z/r + \sum_l W_l(r)P_l$, where z is equal to the number of valence electrons, P_l is the projection operator onto the lth subspace of the spherical harmonics and $W_l(r) = \exp(-\alpha_l r^2) \sum_i C_i^{(l)} r^{n_i^{(l)}}$ [13]. All parameters for O, S and Se atoms are given in the Table A1. The total (pseudopotential) energies for H_2O and H_2S molecules equal to −16.881 a.u. ($B13$ basis set) and −11.121 a.u. ($B11$ basis set), respectively, have been used as a reference in order to define the total energy differences Δ in the Tables 2 and 3. The total energies for O, S, Se and H, atoms were equal to −16.633 a.u., −10.912 a.u., −9.055 a.u. and −0.499 a.u., respectively, when s and/or p-orbitals were expanded into four Gaussians. The parameters of our optimized-in-molecules "double zeta+polarization" basis sets for H_2O, and H_2Se are given in Table A2. It is important to note that those bases are valid only for the pseudopotentials given in Table A1.

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