Modeling of the Exchange Repulsion Energy

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The nonempirical force field model (NEMO) has been augmented with a new exchange repulsion model based on a different choice of expansion center. In the new repulsion model, the size of the atoms are estimated from the trace of the local second-order electron density tensor divided with the local valence charge. A set of general atom type dependent parameters are fitted from SCF calculations on different complexes. An exponential form is used to describe the interaction. The new expansion center is chosen as the point where the local electronic dipole is zero, i.e. the center of electronic charge. The model has been tested on a set of intermolecular complexes between the molecules water, ammonia, methylamine, formamide, and urea.

I. Introduction

The interaction between molecules is one of the research fields within chemistry where quantum chemical methods have contributed mostly. Not only have *ab initio* quantum chemical methods made it possible to obtain accurate information about the strength of the interaction between molecules, but we have also obtained an understanding of the forces that governs the interaction between molecules and their importance.[1] It is probably also true that research fields, where the interaction between molecules is of large importance, such as the formation of structures in biochemistry and surface chemistry, formation of liquid and solid phases, the study of chemical processes in condensed phases, and the conformation of polymer molecules in solution, have increased their relative importance within chemical research. The standard way to calculate potential energy surfaces is to use the supermolecular approach. In that approach the interaction energy is defined as the energy difference between the complex and the energy for the monomers. In order to describe the potential surface, one has to perform quantum chemical calculations for various geometries of the interacting systems, and to avoid problems with the basis set superposition error,[2] three calculations for each studied geometry have to be performed. Since the number of studied geometries needed to obtain a reliable intermolecular potential is large and since the computational resources required to study one geometry also are large, this effectively limits the approach to fairly small complexes. The discussion above indicates part of the weaknesses of the *ab initio* supermolecular approach, but the main drawback of this approach is that it provides the interaction energy as a single number. No further physical information is added to the result.

The basis of the NEMO (nonempirical force field model) method is the partitioning of the interaction energy at the Hartree−Fock level into first- and second-order perturbation terms.[3] The method is a compromise between computational efficiency and reliability of the obtained interaction energy between the studied molecules. Formally, the interaction energy is divided into physically recognizable terms that are supposed to add up to the Hartree−Fock energy according to

$$\Delta E_{\mathrm{scf}} = E_{\mathrm{ele}} + E_{\mathrm{ind}} + E_{\mathrm{exch}} \tag{1}$$

where E_{ele} is the electrostatic energy, E_{ind} is the induction energy, and E_{exch} is the exchange repulsion energy. The advantage of this energy partitioning is, apart from the physical interpretation, that each part can be modified and systematically improved according to required accuracy, and that this can be done independently of the other parts. To obtain the total interaction energy a dispersion term is added to eq 1.

$$E_{\mathrm{tot}} = \Delta E_{\mathrm{scf}} + E_{\mathrm{disp}} \tag{2}$$

In the NEMO model each of these energies is calculated from properties obtained from the SCF wave function of the interacting monomers.

Electrostatic. The electrostatic interaction between two molecules A and B, each molecule having a charge distribution density $\rho(\mathbf{r})$, can be calculated from

$$E_{\mathrm{ele}} = \int \rho_{\mathrm{A}}(\mathbf{r}_1) 1/|\mathbf{r}_1 - \mathbf{r}_2| \rho_{\mathrm{B}}(\mathbf{r}_2)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2 \tag{3}$$

A direct evaluation of this expression is too time consuming especially for larger basis sets and/or molecules and is not suitable for generating a large number of points on a potential energy surface. Instead, in the NEMO approach, the charge distributions are represented by a multicenter multipole expansion (MME) describing the molecules.[4] In a similar way, as the electric charge distribution is approximated with electrostatic multipole moments, the response properties of the considered molecules are described with local polarizabilities[5] located on atoms and bond centers. Thus, in the NEMO method each molecule is represented by a set of multipoles and polarizabilities and the evaluation of the electrostatic energy is done as a sum of interactions over such expansions centers. The advantage of using MME lies in the drastic reduction of detail by using point multipoles instead of covering space by basis functions as in quantum-chemical methods.[6,7] The expansion is normally truncated at the quadrupole moment level. For a full description of the procedure used to obtain a MME, where the charge distribution is described with charges, dipoles and quadrupoles

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located at the nuclei and the chemical bonds, see i.e., the book of Margenau and Kestner.[8]

Induction Energy. All molecules interact with an external field through their polarizabilities. The interaction is normally called polarization or induction interaction and lowers the energy of the system and also leads to a modification of the electrostatic moments of the molecules. This process is normally described using the molecular polarizabilities and hyperpolarizabilities. For larger molecules it is more convenient to partition the total molecular polarizability into local contributions as was done with the molecular charge distribution. If $\alpha_{\alpha\beta,i}$ is a component of the local polarizability tensor situated on atom i, and E_β^{tot} is a component of the total electric field experienced by atom i, then the induced dipole moments on atom i can be calculated from

$$\mu_{\alpha,i}^{\text{ind}} = \alpha_{\alpha\beta,i} E_\beta^{\text{tot}} \tag{4}$$

The field used in the equation above should include the field from all permanent and induced moments of the charge distributions on other molecules. By including local polarizabilities of the atoms, we will include the major part of the effects from the hyperpolarizabilities to the interaction. A local description[5] of the induced dipole moments is necessary since the one-center description of the polarization effects becomes too crude when the intermolecular distances are smaller than the size of the molecule. The local polarizabilities used earlier are calculated from localized orbitals.[9] It is important to localize the orbitals for calculating local polarizabilities, especially for larger molecular systems. Otherwise, the polarizabilities in the center of the molecule would become too small and the polarizabilities on the outer atoms would be too large.

Dispersion Energy. The dispersion energy was estimated using a London-type formula[10]

$$E_{\text{disp}}^{\text{Lon}} = -\sum_{mn}^{\text{atoms}} f_{mn} \frac{CE_{12}}{4} \sum_{ijkl}^{3} \alpha_{ij}^{m}\ \alpha_{kl}^{n} T_{ik} T_{jl} \tag{5}$$

where α is a component of the local polarizability discussed above, T_{ik} is a component of the interaction tensor $\nabla\nabla(1/r)$, C is a constant of 1.89 calibrated from a second-order Möller–Plesset (MP2) calculation,[11] E_{12} is the average molecular excitation energy, and f_{mn} is a site–site damping function, introduced according to Tang and Toennis[12] in order to estimate the effects from overlap of charge distributions. The damping function is characterized by a Born–Mayer parameter, b_{mn}, which is approximated by the size of the atoms as

$$r_m = [\text{Tr } Q_m/q_m]^{1/2} \tag{6}$$

Tr Q_m is the trace of the second moment tensor at center m and q_m is the valence charge at the center. The Born–Mayer parameter b_{mn} is then calculated as

$$b_{mn} = \frac{1}{c(r_m + r_n)} \tag{7}$$

c is estimated from the H_2 system and given the value of 0.1734.[12] The dispersion formula in eq 5 was then adapted to a less complex form which was used in the construction of potentials

$$E_{\text{disp}}^{\text{pot}} = \sum_{mn}^{\text{atoms}} \frac{d_{mn}}{r^{6}_{mn}} S(r_{mn}) \tag{8}$$

$S(r_{mn})$ is a modified form of the damping function including a parameter a, which has to be fitted together with d_{mn}. The a and d parameters were fitted by a least-squares method between eqs 5 and 8. For further details about the previous NEMO model, see the report by Åstrand *et al*.[13]

It is obvious from the approximations discussed above that the main error in the quantum chemical estimates originates from the estimates of the dispersion energy, whereas the SCF interaction energies are close to the Hartree–Fock limit values.

II. Exchange Repulsion

When the distance between two atoms decreases, their electron clouds approach each other and their charge distributions gradually overlap. The Pauli exclusion principle prohibits all the electrons from occupying the overlap region and so reduces the electron density in this region. The positively charged nuclei of the atoms are then incompletely shielded from each other and therefore exert a repulsive force on each other. Thus the electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction.

In the NEMO model,[3] the repulsion energy is defined as

$$E_{\text{rep}} = \Delta E_{\text{scf}} - E_{\text{ele}} - E_{\text{ind}} \tag{9}$$

ΔE_{scf} is the SCF interaction energy corrected for the basis set superposition error (BSSE) by the counterpoise method[2] and E_{ele} and E_{ind} are the electrostatic and induction energies from above. This means that the entity that is called repulsion energy in the NEMO model contains not only the exchange repulsion but also the overlap corrections to the electrostatic and induction energy. One can show, on a theoretical basis,[8] that the exchange repulsion connected with the overlap between two orbitals behaves as $S^2/(1 + S^2)$ which can be Taylor expanded as $\alpha S^2 + \beta S^4 + \gamma S^6 + ...$, where S is the overlap of the orbitals in the different molecules. The previous repulsion model[13] in the NEMO approach was based on this and in the model the repulsion energy was expanded according to

$$E_{\text{rep}} = \sum_{mn}^{\text{atoms}} \alpha_{mn}\Theta_{mn} + \beta_{mn}{\Theta_{mn}}^{2} + \gamma_{mn}{\Theta_{mn}}^{3} \tag{10}$$

where Θ_{mn} includes overlap integrals and α_{mn}, β_{mn}, and γ_{mn} are atom type parameters fitted from calculations on small dimer complexes. The form of eq 10 was then fitted to a simpler atom–atom potential function which was used in the simulations.

$$E_{\text{rep}} = \sum_{ij}^{\text{atoms}} f_{ij}\ \mathrm{e}^{-g_{ij}} + \left(\frac{h_{ij}}{r_{ij}}\right)^{n} \tag{11}$$

The pair parameters have been fitted from complex geometries with large repulsion energies. The disadvantage with this repulsion model is that we need the overlap integrals in eq 10 and that we further need to do an additional fitting to find the form of eq 11. This additional fitting has to be done for each complex one would like to study. Instead, one would like to have a simpler expression which does not include the overlap integrals and the additional fitting procedure indicated by eq 11. The behavior of the repulsion should give a high penalty of the functional form at short distances, and exponential behavior at moderate and long distances.[8] It should contain information about the size of the atoms and the number of electrons. For simulation purposes we would like to have spherical atom–atom interactions. The functional form of the repulsive interaction between two atoms *i* and *j* chosen by us has the form

$$E_{ij}^{\mathrm{rep}} = \Gamma_{ij} \mathrm{e}^{-\Lambda_{ij}\Theta_{ij}} + \left(\frac{\tilde{r}_i + \tilde{r}_j}{R_{ij}}\right)^{21} \tag{12}$$

where Θ_{ij} is a measure of the effective distance of the charge distributions between atom *i* and atom *j*, and Γ_{ij} and Λ_{ij} are some atom type dependent fitting parameters. This expression has the same form as eq 11. However, the parameters are calculated in a different way. The last term on the right-hand side of eq 12 is added to ensure a high repulsion at very short distances. $\tilde{r}_i$ and $\tilde{r}_j$ are atom-dependent parameters which are adjusted from the fairly strong hydrogen bonded water−water and formamide−water complex to give the right structure and energy. The parameters behave as radii for the atoms in order to compensate for the exponential form of the repulsion at shorter distances. R_{ij} is the real distance between the atoms. This will of course give too steep a repulsion at short distances, but the idea is that this term should only give significant contributions where the repulsive part of the interaction dominates the interaction. The quantity Θ_{ij} in eq 12 is a measure of the effective distance between the charge distributions of atoms *i* and *j* and is defined as

$$\Theta_{ij} = [\mathbf{R}_{ij}^{\mathrm{T}} \mathbf{M}_{ij}^{-1} \mathbf{R}_{ij}]^{1/2} \tag{13}$$

where $\mathbf{M}_{ij}$ is defined as

$$\mathbf{M}_{ij} = \frac{\mathbf{Q}_i}{q_i^{\mathrm{v}}} + \frac{\mathbf{Q}_j}{q_j^{\mathrm{v}}} \tag{14}$$

and is a measure of the extensions of electron density around atoms *i* and *j*. $\mathbf{Q}_i$ is the local contribution to the second moment of electrons located to atom *i* and q_i^{v} is the corresponding valence charge. Equation 14 resembles very much the definition of the Born−Mayer parameter in eq 7. The motivation for the choice of eq 14 is seen from the definition of the second moment of the electron density.

$$\mathbf{Q} = \int_V \rho(\mathbf{r})\mathbf{r}\cdot\mathbf{r}^{\mathrm{T}}\, d\mathbf{V} \tag{15}$$

According to eq 15 this quantity is proportional to $\mathbf{r}^2$ but also to the number of electrons. With the definition made in eq 14, Θ_{mn} will give an estimate of the extension of the electronic cloud connected to an atom which is independent of the number of electrons associated with the two atoms. If we assume spherical atom−atom interactions, *i.e.*, isotropic charge distributions, then eq 14 can be rewritten as

$$M_{ij} = \frac{\mathrm{Tr}(\mathbf{Q}_i)}{q^{\mathrm{v}}{}_i} + \frac{\mathrm{Tr}(\mathbf{Q}_j)}{q^{\mathrm{v}}{}_j} \tag{16}$$

and the effective distance Θ_{ij} as

$$\Theta_{ij} = [|\mathbf{R}_{ij}|^2/M_{ij}]^{1/2} \tag{17}$$

$\Lambda_{ij} = 1/(\alpha_i + \alpha_j)$, where α_i is a fitted parameter and measures the effective "size" of atom *i*. Λ_{ij} measures at which intermolecular distance the overlap between two atoms becomes important. Γ_{ij} in eq 12 equals $\Gamma_{ij} = q_i^{\mathrm{v}} q_j^{\mathrm{v}} \kappa_i \kappa_j$, where κ_i and κ_j are fitted parameters depending on atom type. Γ_{ij} takes care of the fact that atoms with more electrons should give more repulsion. The expression in eq 12 leaves us with two independent parameters for each atom type to be optimized, α and κ. The atomic type dependent parameters, α and κ, are fitted from a test set of SCF calculations on small dimer complexes. Once we have found α and κ, then we can use them in any molecular system without any further fitting. This is the fundamental idea of this repulsion model.

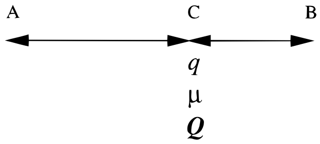

Figure 1. Three-center model of the charge distribution. Atoms A and B defines the bond center C. The moments on C are divided between A and B.

A. Charge Modeling. The formulation of the exchange repulsion model above forces us to introduce some modifications compared to earlier NEMO models[3,13] in order to optimize the model. To find the physically most appropriate values for α and κ, we need an as good description as possible of the charge distribution with as few parameters as possible. The modifications introduced are

(1) conversion from atom and bond to atom model; (2) removal of the quadrupole moment in the calculation of the electrostatic and induction energy; and (3) transfer of the MME center to the center of the local electron charge distribution.

1. Atom Model. This item has no physical origin but it is introduced in order to reduce the number of parameters in the model. When this simplification is introduced, there will only be two parameters for each type of atom in the model. The simplification means that the electrostatic moments, located to the center of a bond, are moved to the atoms that define the bond. Figure 1 illustrates how the moments associated with the center of the bond in the atom and bond model are partitioned to the atoms defining the bond. If we label the atoms A and B and the corresponding bond center C, then the fraction of the moments that is divided between A and B is decided by the distance of the center to the atoms A and B. The contribution of the moments from C to A can be calculated from

$$\text{charge} \qquad q_A = q\left|\frac{\mathbf{r}_{CB}}{\mathbf{r}_{AB}}\right|$$

$$\text{dipole} \qquad \mu_{\alpha,A} = \underbrace{q_A r_{\alpha,CA}}_{\text{omitted in earlier model}} + \mu_\alpha \left|\frac{\mathbf{r}_{CB}}{\mathbf{r}_{AB}}\right|$$

$$\text{second moment} \qquad Q_{\alpha\beta,A} = q_A r_{\alpha,CA} r_{\beta,CA} + \underbrace{(\mu_{\alpha,A} r_{\beta,CA} + \mu_{\beta,A} r_{\alpha,CA})}_{\text{omitted in earlier model}} + Q_{\alpha\beta}\left|\frac{\mathbf{r}_{CB}}{\mathbf{r}_{AB}}\right|$$

where we have used the following notations: *q* for the charge in the bond, μ for the dipole, and *Q* for the second moment, $\mathbf{r}_{\mathrm{CB}}$ is the distance vector from bond center C to atom B, $\mathbf{r}_{\mathrm{CA}}$ the corresponding distance from bond center C to atom A, and $\mathbf{r}_{\mathrm{AB}}$ is the distance from atom A to atom B. $r_{\alpha,\mathrm{CA}}$ is a component of the distance vector. $\mu_{\alpha,\mathrm{A}}$ and $Q_{\alpha\beta,\mathrm{A}}$ are components of the contribution to the dipole moment and the second moment tensor to atom A. The same procedure is used for the partitioning of the bond center moments to atom B. In the earlier two-center NEMO model,[13] the contribution from the charge to the dipole moment and the contribution from the dipole to the second moment were omitted since they summed up to a zero contribution to the total moments of the molecule. However, we have realized that we have to include these parts as well in order to improve the physical description of the charge distribution. This division of the moments on C to the atoms A and B will preserve the total moments for the molecule just as the old partitioning scheme. The polarizabilities located on the bond site will be divided equally between the two atoms constituting the bond.

2. Modeling the Quadrupoles as Dipoles. To speed up the evaluation of the intermolecular potential even more, the quadrupole moment tensor on each atom is removed and the dipoles of the neighboring atoms are modified in such a way that the total quadrupole moment of the molecule is preserved. The motivation for this simplification is a wish to reduce the time needed to calculate the electrostatic and induction energies (we still need the trace of the second moment tensor for modeling of the exchange repulsion). The procedure where the quadrupoles are removed is based on an iterative scheme, where initially the quadrupole moment on an atom is modeled with dipoles on the atoms bonded to the considered atom. If some part of the quadrupole moment cannot be removed with dipoles on these nearest neighbors, then a set of next nearest neighbors are used to remove the remaining part, and then the nearest ones are used again in an iterative scheme. If, which could happen, there exists a component of the quadrupole moment that cannot be modeled in this way, then this component is disregarded. This could happen in systems with atoms with locally high symmetry in an unsymmetric molecule.

3. Choice of New Centers. Normally the atoms are used as expansion centers for intermolecular potentials. We will below give reasons for changing this choice. The interaction between two sites in an intermolecular potential normally consists of several terms with different distance dependence. There is, however, one term that varies faster with the site−site distance than the other terms. This is the exchange repulsion term. This term originates from the overlap between the electron clouds of different atoms. If we analyze the local charge distribution around an atom we see that the valence electrons, which are the main origin behind this force, are slightly displaced relative the considered atom. Similar ideas have previously been used to model the exchange interaction between two HCl molecules, where the asymmetry of the electronic cloud around the Cl atom is of importance for the exchange repulsion between the molecules.[14] Thus, it seems reasonable to move the expansion center to the center of valence electronic charge, i.e., the point where the local dipole moment vanishes. (It is assumed that it is the valence electrons on the atom that are moved.) In the multicenter multipole expansion mentioned above, the electrostatic and response moments are centered around the nucleus. This in turn means that when we fit the parameters α and κ, where we try to estimate the effective electronic charge radius and where the distances between the atoms are crucial, we will not use the interatomic distances. Instead, the distances should be measured from the electronic charge center of each atom, because it is the electronic charge distributions that interact with each others, as described above. This should give a better physical picture of what happens when two atoms interact. In practice, this means that the MME centers are moved from the nucleus, in the opposite direction of the dipole (the dipoles are defined to go from − to +) and to the center of the charge distribution, i.e., where the dipole moment for the electrons located to the atom is zero. These new centers should give a better fitting of α and κ. The displacement of the MME center is performed in such a way that the total local moments of the molecule are preserved.

The displacement vector $\Delta\mathbf{r}$ of the MME center is defined as

$$\Delta r_{\alpha,i} = -\mu_{\alpha,i}/q_i^{\mathrm{v}} \qquad (18)$$

where $\mu_{\alpha,i}$ is a component of the dipole moment on MME center i and $q^{\mathrm{v}}{}_i$ is the valence charge of the center.

The corrections to the different moments due to this displacement must be done in two steps. The first step involves the correction of the dipole moment and the second moment to be used in the electrostatic and inductive part of the energy. Here we use the net charge in the calculation of the energies. In the exchange repulsion part we need the valence charge and hence have to correct the second moment with respect to that (the dipole becomes zero). This means that we have two slightly different second moment models when we calculate the interaction energy. The corrections to the dipole and second moment in component form, in the case of electrostatic and induction, becomes

$$\Delta\mu_{\alpha,i}^{\mathrm{el,ind}} = \Delta r_{\alpha,i} q_i^{\mathrm{n}} \qquad (19)$$

$$\Delta Q_{\alpha\beta,i}^{\mathrm{el,ind}} = q_i^{\mathrm{n}} \Delta r_{\alpha,i} \Delta r_{\beta,i} + \mu_{\alpha,i} \Delta r_{\beta,i} + \Delta r_{\alpha,i} \mu_{\beta,i} \qquad (20)$$

q_i^{n} is the net charge on site i. In the correction to the repulsive part, we have to move the whole valence charge, q_i^{v}, to the new center. Note that the second moments are explicitly used in the evaluation of the exchange interaction, but only modeled with dipoles for the description of the electrostatic interaction. The correction to the second moment will be

$$\Delta Q_{\alpha\beta,i}^{exch} = q_i^{v} \Delta r_{\alpha,i} \Delta r_{\beta,i} + \mu_{\alpha,i} \Delta r_{\beta,i} + \Delta r_{\alpha,i} \mu_{\beta,i} \qquad (21)$$

$$= {}^1\!/_2 (\underbrace{q_i^{v} \Delta r_{\alpha,i}}_{-\mu_{\alpha,i}} \Delta r_{\beta,i} + \Delta r_{\alpha,i} \underbrace{q^{v}{}_i \Delta r_{\beta,i}}_{-\mu_{\beta,i}}) + \mu_{\alpha,i} \Delta r_{\beta,i} + \Delta r_{\alpha,i} \mu_{\beta,i}) \qquad (22)$$

$$= {}^1\!/_2 (\mu_{\alpha,i} \Delta r_{\beta,i} + \Delta r_{\alpha,i} \mu_{\beta,i}) \qquad (23)$$

The introduced modifications as described above will slightly modify the electrostatics and induction as well. Maybe the best argument for this choice of new centers is the fact that the obtained fittings are of much higher quality than those obtained with the nuclei as expansion centers (see below).

III. Results

A. Fitting of Parameters. Given the functional form in eq 12 for the estimate of the repulsion energy and with the modifications introduced above, we can now determine the parameters α and κ by fitting eq 12 to a proper expression. The parameters were determined by minimizing the following equation:

$$\mathrm{error} = \sum_i (\mathrm{e}^{(0.15(E_{\mathrm{rep},i}^{\mathrm{est}} - E_{\mathrm{rep},i}))} - 1)^2 \times \mathrm{weight} \qquad (24)$$

where i sums over a test set of small dimer complexes. $E_{\mathrm{rep},i}$ is the repulsion energy, eq 12, without the hard-core repulsion and the weight = min(2, $\mathrm{e}^{-\Delta E_{\mathrm{scf},i}/5}$), where the 2 was used as an upper limit for the weight and the factor 1/5 in the exponent was chosen in order to favor deep-lying energies (atomic units are used in the fitting). $E_{\mathrm{rep}}^{\mathrm{est}}$ is defined as

$$E_{\mathrm{rep}}^{\mathrm{est}} = \Delta E_{\mathrm{scf}} - E_{\mathrm{ele}} - E_{\mathrm{ind}} \qquad (25)$$

which is the same as eq 9. The test set of small dimer complexes contains 463 geometries and energies (ΔE_{scf} in eq 25) for the molecules ammonia, ether, ethene, formaldehyde, acetone, urea, water, and formic acid. ΔE_{scf} is corrected for

TABLE 1: Fitted Parameters α and κ as a Function of Different Changes Introduced in the Model[a]

model		C(sp^3)	C(sp^2)	O(sp^3)	O(sp^2)	N	H	H[b]	error[c]
1	α	0.7600	0.2184	0.2048	0.3459	0.3248	0.1485	0.1712	57.55
2	α	0.5009	0.2056	0.2474	0.2267	0.2705	0.1376	0.1666	24.61
3	α	0.5572	0.2028	0.2326	0.2797	0.3462	0.0975	0.1562	18.59
4	α	0.3431	0.2288	0.2508	0.2774	0.3404	0.0991	0.1032	7.62
4′	α	0.3134	0.2279	0.2521	0.2741	0.3182	0.1140	0.1176	6.71
5	α	0.2586	0.2176	0.1764	0.1724	0.1376	0.3284	0.1242	4.77
5′	α	0.2551	0.2222	0.1827	0.1797	0.1431	0.3154	0.1378	4.53
1	κ	0.3030	37.7375	81.4610	7.9574	6.8812	528.3287	81.1661	
2	κ	1.0525	32.9051	15.7313	28.2959	9.7349	438.3507	55.6754	
3	κ	0.4834	34.2079	28.0886	11.2147	3.6264	808.5646	91.9784	
4	κ	3.9251	21.4236	18.8140	11.7882	4.3292	537.4425	284.4447	
4′	κ	5.7772	21.0390	17.6984	12.2386	5.8260	434.3446	224.6350	
5	κ	12.7346	26.2294	89.0004	89.1566	179.0901	9.1185	251.8265	
5′	κ	13.5221	23.5890	72.8919	71.6759	147.0186	12.1640	169.2679	

[a] The different changes are given in the text. Polarizabilities calculated from localized orbitals (ref 9) have been used in all calculations except the first, 4′ and 5′. α is given in au and κ will give the energy in kcal/mol. [b] Hydrogen connected to carbon atoms. [c] Total error in eq 24. The total weight of the error, i.e., the sum of weight in eq 24, is 373.70.

the basis set superposition error with the counterpoise method.[2] In all SCF calculations we used the MOLCAS package[15] with atomic natural orbitals (ANO) basis functions.[16] For the carbon, nitrogen, and oxygen atoms, a [10/6/3] primitive basis was contracted to (4/3/2). For hydrogen atoms bonded to polar atoms, such as nitrogen and oxygen, a [6/4] set contracted to (3/2) was used, and for hydrogen atoms bonded to nonpolar atoms, such as carbon, we used [6/3] contracted to (3/1). The value 0.15 in eq 24 was found by adjustment to give a good low-energy fit and still provide reasonable results for the repulsive regions.

The damping function in the expression for the dispersion energy, eq 5, damps the interaction energy equally in all directions. This means that we will have an equal damping in directions with small polarizabilities as well as in directions with large polarizabilities. In cases with strongly anisotropic polarizabilities this often corresponds to an unisotropic extension of the charge distribution around the atom. For such situations one would prefer a nonspherical damping of the dispersion interaction. This possibility is not investigated in this work. Another problem concerning the polarizabilities is constituted by the way the polarizabilities initially associated with a bond are divided between the two atoms defining the bond. In our model the polarizability of the bond is divided equally between the two atoms in the conversion from an atom and bond model to an atomic model. Due to the very small intermolecular distances for hydrogen-bonded systems this may cause problems. If we consider an ordinary linear hydrogen-bonded system X−H Y, where X and Y are electronegative atoms (O,N) and X acts as hydrogen bond donor and Y as acceptor, then the distance between Y and H will normally be 2 Å and the distance between Y and the midpoint of the X−H bond 2.5 Å, whereas the X−Y distance is 3 Å. Normally, the polarizability associated with the bond is twice as large as the polarizability associated with the H atom. If we identify the Y atom with a dipole and calculate the interaction between the dipole and the polarizability when it is located in the bond and when it is distributed to the two atoms, we can see that the interaction is roughly twice as large when the polarizability is divided between the two atoms. Furthermore, it is equally large as the original contribution from the hydrogen atom. We can thus see that we will overestimate the induction and dispersion interaction with models where the bond polarizabilities are distributed to the atom. In earlier NEMO model,[13] this problem was overcome by making an additional fit to the form in eq 8 which will take care of the problem with anisotropic polarizabilities and the partitioning of the bond polarizabilities. To solve this problem, we use isotropic polarizabilities description which is consistent with the damping model and easier to work with in simulation of larger systems.

Several changes have been introduced in the way we model the charge distribution for a molecule compared to the previous model.[13] How have these changes affected the model and how much has each modification contributed to the improvement of describing the charge distribution and the repulsion? To highlight these questions, we have, in a systematic way, changed the conditions used in the fitting of the repulsion parameters. The most important models are listed below and the results are presented in Table 1.

Model 1. The old NEMO mode.

Model 2. Improvement of the atom model.

Model 3. Movement of the MMP centers to the center of valence electronic charge.

Model 4. Isotropic second-order moments are used for the description of the repulsion.

Model 4′. Like model 4, but with polarizabilities from nonlocalized orbitals.

Model 5. Isotropic polarizabilities.

Model 5′. Isotropic polarizabilities with polarizabilities from nonlocalized orbitals.

Table 1 shows the results from the different models. The changes listed above are added to the previous model so that, e.g., model 5 includes all the changes introduced in models 2−4. In all models above, except the first one, 4′, and 5′, we have used polarizabilities from localized orbitals. Åstrand and Karlström[9] investigated the effect of using polarizabilities from localized orbitals and we were interested in this effect on the present repulsion model.

Model 1. This is the old NEMO model,[13,17] with the atoms as multicenter multipole expansions centers and with anisotropic second moments and polarizabilities. We use this as our reference model in order to study the effects of the introduced changes.

Model 2. Here we improve the atomic model by including the omitted contributions to the dipole and second moment in the conversion from an atom−bond model to an atom model. This improved the fitting of the repulsions parameters by a factor of 2.

Model 3. We move the MMP centers to the center of valence electronic charge. This action makes an improvement to the fitting error by a factor of 1.3.

Model 4. When we introduce isotropic second-order charge distributions to model the repulsion energy, the error went down with a factor of 2.5.

TABLE 2: Four-Parameter Repulsion Parameters for Some of the Models from Above[a]

model		C, O, N	H	error
4′	α	0.2792	0.0801	10.36
5	α	0.2560	0.1211	10.70
5′	α	0.2568	0.1182	10.25
4′	κ	11.4655	803.1087	
5	κ	15.9841	323.8845	
5′	κ	15.8973	338.8630	

[a] One α/κ for C, O, and N and one α/κ for H. α is given in au and κ will give the energy in kcal/mol. The error in the table is the error in eq 24. The total weight of the error is the same as in Table 1.

Model 4′. We tested model 4 by using polarizabilities from nonlocalized orbitals and found that the fitting improved a bit.

Model 5. The last change introduced by us is to use isotropic polarizabilities in the model.

Model 5′. Model 5 was tested with polarizabilities from nonlocalized orbitals. The fitting improved in this case as it did in model 4′. The advantage of using polarizabilities from localized orbitals is not seen. The two polarization models are almost equivalent but we will use the parameters obtained from the localized model, since we are convinced that the localization scheme will be necessary for larger system.

It is clear from Table 1 that it is important to have an as good and realistic description of the charge model as possible when modeling the repulsion parameters. Comparing the old NEMO model in Table 1 with model 5, which is the model we will use, the error has decreased by a factor of 12. For simulation purposes it is very promising that the fitting is better for the isotropic polarizabilities and charge distributions. One effect which is notable is that the α for the sp^3 carbon is much larger than for the sp^2 carbon. This effect is due to that the sp^3 carbon is surrounded by four atoms which will prevent a closer approach to the sp^3 carbon. For this reason, the repulsion parameters for this atom will not be as important as it is for the other atoms.

The number of parameters are reduced considerable in this report. Two atom type parameters for each atom in the repulsion model makes a total of 14 parameters to bookkeep for the system in this study. If one looks at the parameters in Table 1, one can divide α and κ into two groups according to their sizes: one group containing the atoms C, O, and N and one group containing only H. It would be appealing if we could fit one set of parameters for these two groups. This should reduce the number of parameters even more and give us only four parameters to bookkeep. Table 2 shows α and κ for a four-parameter fit for the three best fits in Table 1. The parameters for C, O, and N are very close to the mean values of the corresponding parameters in Table 1. The error for this four-parameter fit is of course larger than the corresponding fit for the parameters in Table 1, but the profile and the error of the fit are still very good. This implies that the charge model which we have introduced contains some physical relevance.

The water dimer potential is very flat in the energy minima and small changes in the parameters will shift the geometry in the energy minima to a large extent. For this reason and since the water dimer is a strong hydrogen-bonding system, the water dimer was used to adjust the short-range repulsion parameters $\tilde{r}_\alpha$ and $\tilde{r}_\beta$ in eq 12 together with formamide. The atom-dependent parameters $\tilde{r}_\alpha$ and $\tilde{r}_\beta$ are shown in Table 3 for two cases, model 4′ and model 5 in Table 1. As can be seen, the radius of the oxygen and the hydrogen atom is smaller in the case of isotropic polarizabilities, showing that the parameters for model 5 in Table 1 gives more repulsion than the parameters in model 4 where we use anisotropic polarizabilities. As a matter of fact, we get very good geometry and energy for the water dimer and the formamide complex without the short-range parameters in eq 12, but to be on the safe side and toensure a high repulsion at very short distances, these parameters are included. The radius for the carbon atom is set to zero since it is never involed in any strong polar bonds. The most important parameters are those for oxygen and hydrogen which will interact strongly and contribute significantly to the total interaction energy if coming to close to each other.

TABLE 3: Atom-Dependent Short-Range Parameters[a]

model		C	O	N	H
4′	$\tilde{r}$ (au)	0.00	1.79	1.29	1.93
5	$\tilde{r}$ (au)	0.00	1.70	1.29	1.60

[a] Adjusted from water−water and formamide−water complex for two of the models from above.

B. Potential Functions. To test the reliability of the parameters α and κ we used two groups of complexes and compared the potentials obtained with the NEMO model with BSSE-corrected[2] *ab initio* SCF calculations. The first group consist of molecules included in the test set in which the parameters have been fitted, and the second group includes molecules not included in the test set. The molecules in the first group consist of water and urea and the second group includes formamide and methylamine in complex with water and ammonia. The last group will give us a hint of how general our parameters are. For the exchange repulsion the full expression of eq 12 has been employed including the short-range repulsion parameters from model 5 in Table 3. We have tested the parameters from both models 4′ and 5 in Table 1 and the corresponding reduced four-parameter form in Table 2. The potential with repulsion parameters from the anisotropic polarizabilities, model 4′ in Table 1, is named ANISOTROP NEMO, referring to their being calculated using anisotropic polarizabilities, and the potential with the repulsion parameters from model 5 in Table 1 is named NEMO. All complex structures given here are optimized by minimizing the total interaction energy in eq 2 and by considering the monomers as rigid molecules and only vary their relative positions and orientations. The optimized geometries used in constructing the potentials were calculated with the parameters from model 4′ in Tables 1 and 3. All potentials are given as a function of the center of mass distance. The structure of the water monomer is taken from the paper of Matsuka et al.[18] whenever it is used below.

Water Dimer. The water dimer is a very useful and important molecular system to test a model with. Its importance in biological systems cannot be overestimated and a lot of theoretical work has been done on it.[19−25] This makes the water dimer suitable to use as a test molecule in order to compare the results obtained with the present NEMO model with previous *ab initio* calculations.

A translinear C_s dimer structure (Figure 2) was obtained which is in agreement with experiments[26] and *ab initio* calculations.[20,21,27] The interaction energy, in Figure 3 and Table 4, is given as a function of the distance between the mass centers of the molecules and one can notice the steep behavior on the inside of the potential well for the ANISOTROP NEMO compared to the SCF points. This behavior is, as we mentioned before, due to the short-range repulsive part in eq 12 which is more characteristic for the ANISOTROP NEMO. The NEMO potential behaves smooth and fine compared to the SCF points and so does the potential with the reduced four-parameter model,

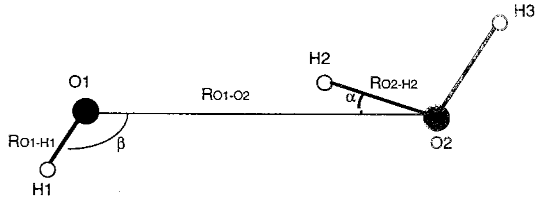

Figure 2. Translinear C_s geometry of the water dimer in the energy minima.

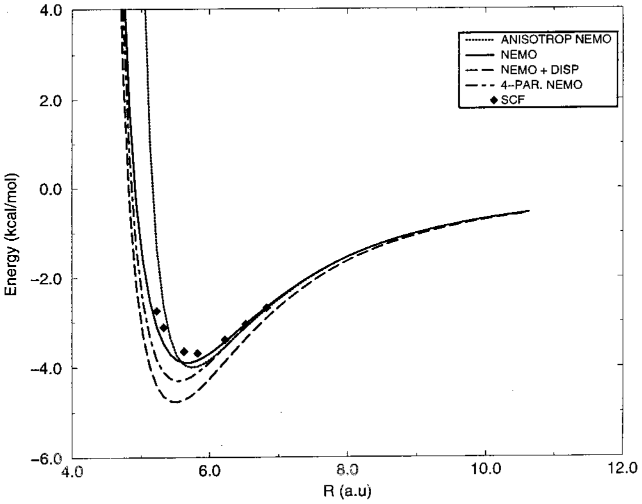

Figure 3. Water dimer interaction energy.

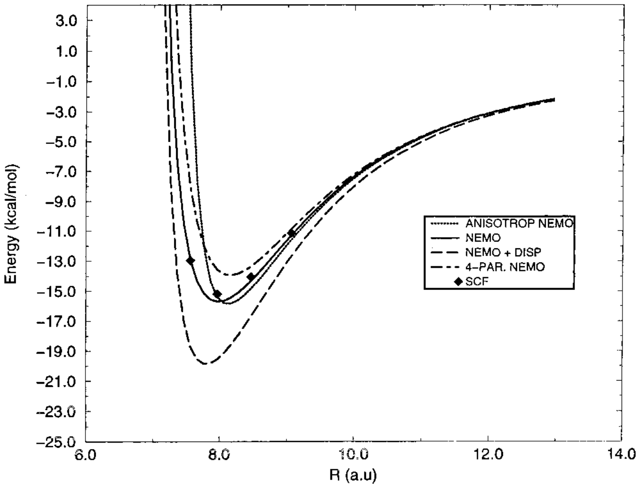

Figure 4. Interaction energy of the cyclic urea dimer as a function of the distance between the center of masses.

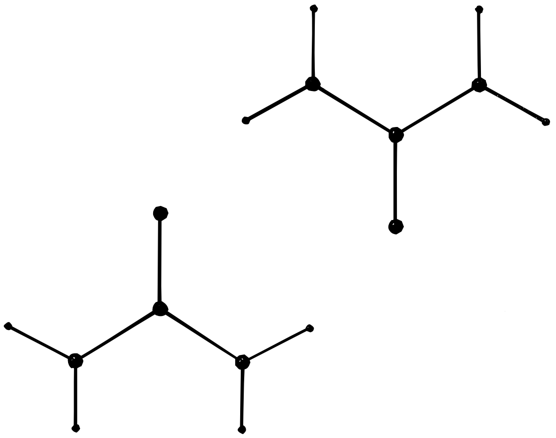

Figure 5. Structure of the cyclic urea dimer in the potential minimum.

however, with a slightly deeper minimum. The nice fit of the reduced four-parameter potential indicates that the way we model the charge distribution contains some physical relevance. As for the geometry and the total energy, the results lie well in the range of extensive *ab initio*[19−22,24] calculations. Our O−O distance and dimer energy are very similar to corresponding data obtained from other theoretical cqalculations (see Table 4). The parameters in Table 3 where used to tune the O−O distance and interaction energy. The energy for the water dimer with parameters from model 5 in Table 1 and optimized without the short-range parameters is −4.85 kcal/mol and R_{O-O} = 2.88 Å (distance between the atomic centers) which shows the small influence of the short-range parameters in Table 3 and the stability of the repulsion parameters α and κ. The corresponding energy and distance are shown in Table 4.

Urea−Water/Urea−Urea. Urea is one of the smallest biologically important molecules. It is well-known for its high solubility in water, its usage as protein denaturant, and as a mammalian waste product. Urea may also be considered as a model for interactions present in a peptide bond. An accurate description of the urea interaction is thus of great importance.

The urea monomer structure is taken from the paper of Andrew and Hundman.[28] For the urea dimer we found the linear (Figure 5) as well as the cyclic urea dimer structure, reported elsewhere,[13] but we will only focus on the cyclic structure here since it is the global minimum geometry. The urea−water complex (Figure 7 and Table 6) is the same as the one obtained with the old NEMO model.[13] Both the urea−water potential (Figure 6) and the urea dimer potential (Figure 4) display the same steep short-range repulsion behavior on the inside of the potential well for the ANISOTROP NEMO as seen in the water dimer, while the NEMO potential behaves smooth and fine. The agreement with the SCF points close to the potential energy minima is better than ±0.5 kcal/mol except for the reduced four-parameter potential for the urea−water complex where the difference is about 1 kcal/mol. The corresponding four-parameter potential for the urea dimer is almost on top on the SCF and NEMO potential and further confirms our charge model. The contributions from the electrostatic and dispersive

TABLE 4: Comparison of Geometries and Energies for the Water Dimer[a]

	this work		Åstrand[13]	ASP[25]	Schutz[21]	Mas[32]	expt[26]
R_{O-O} (Å)	2.99[b]	2.90[c]	2.88	2.98	2.94	2.95	2.95
α (deg)	4.0	10.3	4.4	0	4.3	6.8	0
β (deg)	110.8	112.0	121	117	128.2	124	128
E_{int}	−4.96	−4.80	−4.89	−4.68	−4.98	−5.2 ± 0.70	−5.4 ± 0.70
E_{ele}	−6.01	−6.74	−6.89	−5.64			
E_{ind}	−0.70	−0.67	−0.87	−0.89			
E_{rep}	2.77	3.64	4.23	3.93			
E_{disp}	−1.02	−1.02	−1.18	−2.09			

[a] All energies are given in units of kcal/mol. The R_{O-O} distances are between the atomic centers. [b] Geometry optimized with parameters from model 4′ in Table 1. [c] Geometry optimized with parameters from model 5 in Table 1.

TABLE 5: Energies for the Cyclic Urea Dimer at the Energy Minimum (kcal/mol)[a]

	this work		Åstrand[13]	
	aniso par[b]	iso par[c]	early model[f]	new model[g]
$R(O_u-H_w)$ (Å)[d]	2.01	1.88	1.92	
$R(O_u-H_w)$ (Å)[e]	2.07	1.95		1.98
$R(O_w-H_u)$ (Å)[d]	2.22	2.17	1.98	
$R(O_w-H_u)$ (Å)[e]	2.31	2.27		1.99
E_{int}	−10.6	−11.1	−11.2	−10.1
E_{ele}	−12.9	−14.6	−16.2	−16.5
E_{ind}	−2.2	−2.1	−3.0	−2.5
E_{rep}	6.8	8.2	10.9	11.9
E_{disp}	−2.2	−2.5	−2.9	−3.0

[a] All energies are given in units of kcal/mol. A comparison is done with the old NEMO model. [b] Repulsion parameters from model 5 in Table 1. [c] Repulsion parameters from model 5 in Table 1. [d] Distance between the atomic centers on the atoms. [e] Distance between the charge centers on the atoms. [f] Early model refers to the work done by Åstrand.[13] [g] New model refers to the geometry used by Åstrand[13] but with the present NEMO model and repulsion parameters from model 5 in Table 1.

TABLE 6: Geometries and Energies for the Urea−Water Complex at the Energy Minimum[a]

	this work		Åstrand[13]	
	aniso par[b]	iso par[c]	early model[f]	new model[g]
$R(O_u-H_w)$ (Å)[d]	2.01	1.88	1.92	
$R(O_u-H_w)$ (Å)[e]	2.07	1.95		1.98
$R(O_w-H_u)$ (Å)[d]	2.22	2.17	1.98	
$R(O_w-H_u)$ (Å)[e]	2.31	2.27		1.99
E_{int}	−10.6	−11.1	−11.2	−10.1
E_{ele}	−12.9	−14.6	−16.2	−16.5
E_{ind}	−2.2	−2.1	−3.0	−2.5
E_{rep}	6.8	8.2	10.9	11.9
E_{disp}	−2.2	−2.5	−2.9	−3.0

[a] All energies are given in units of kcal/mol. A comparison is done with the old NEMO model. [b] Repulsion parameters from model 4′ in Table 1. [c] Repulsion parameters from model 5 in Table 1. [d] Distance between the atomic centers on the atoms. [e] Distance between the charge centers on the atoms. [f] Early model refers to the work done by Åstrand.[13] [g] New model refers to the geometry used by Åstrand[13] but with the present NEMO model and repulsion parameters from model 5 in Table 1.

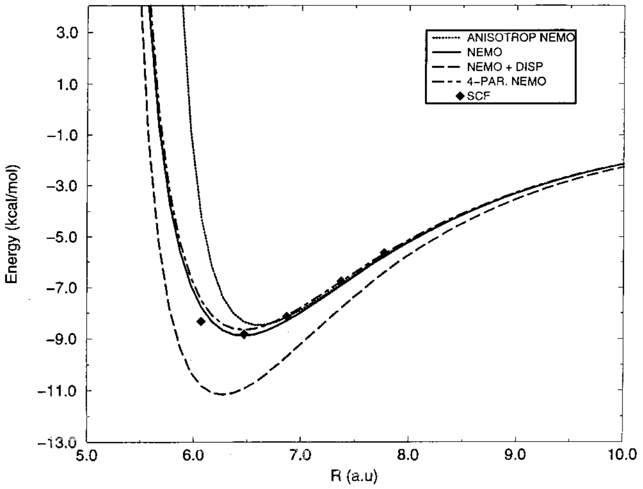

Figure 6. Potential of the urea−water complex as a function of the distance between the center of masses.

parts have not changed considerably despite the modifications in the description of the charge distribution. A small increase of the induction energy is noted in both the urea dimer and the urea−water complex when we compare with earlier work[13] in Table 6.

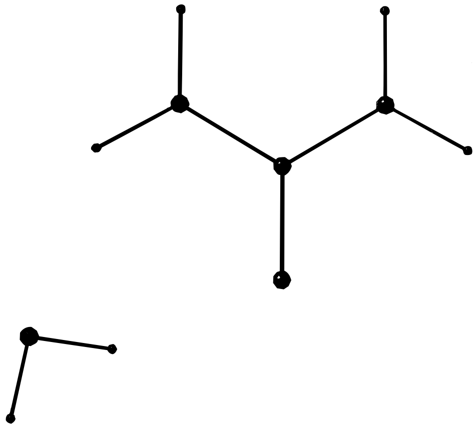

Figure 7. Structure of the urea−water complex in the potential minimum.

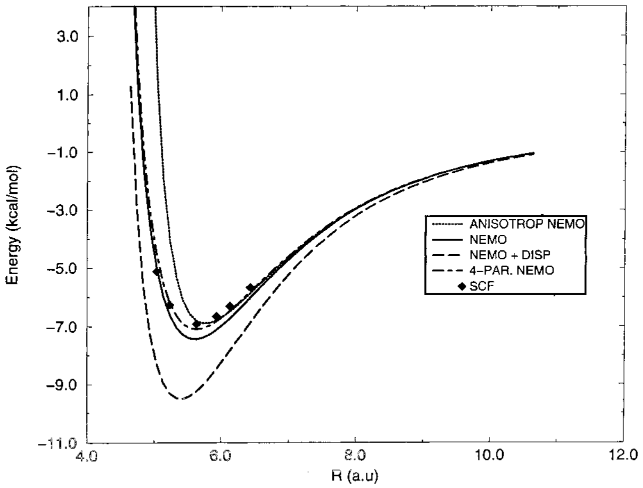

Figure 8. Interaction energy of the formamide−water complex as a function of the distance between the center of masses for structure I.

TABLE 7: Geometries and Energies (kcal/mol) for the Formamide−Water complex at the Global Energy Minimum with Anisotropic and Isotropic Polarizabilities

	this work		Engdahl[17]	
	aniso par[a]	iso par[b]	early model[e]	new model[f]
$R(O_F-H_w)$ (Å)[c]	2.06	1.92	2.21	
$R(O_F-H_w)$ (Å)[d]	2.12	1.98		2.26
$R(O_w-H_F)$ (Å)[c]	2.26	2.20	1.91	
$R(O_w-H_F)$ (Å)[d]	2.34	2.28		1.99
E_{int}	−8.50	−9.52	−8.25	−8.52
E_{ele}	−10.55	−12.16	−12.13	−11.96
E_{ind}	−1.45	−1.61	−2.10	−1.52
E_{rep}	5.21	6.53	8.17	7.26
E_{disp}	−1.70	−2.28	−2.18	−2.17

[a] Repulsion parameters from model 4′ in Table 1. [b] Repulsion parameters from model 5 in Table 1. [c] Distance between the atomic centers on the atoms. [d] Distance between the charge centers on the atoms. [e] Early model refers to the work done by Engdahl.[17] [f] New model refers to the geometry used by Engdahl[17] but with the present NEMO model and repulsion parameters from model 5 in Table 1.

Formamide−Water. The importance of formamide lies in the fact that it is the simplest molecule which contains an amide group. An important aspect of the chemistry of amides is that they provide the structural unit characteristic for the peptide bond in proteins. Formamide has also been used to tune the parameters $\tilde{r}_\alpha$ and $\tilde{r}_\beta$ in Table 3.

The structure for the formamide monomer is taken from the paper of Kitano and Kuchitsu.[29] The geometry optimization

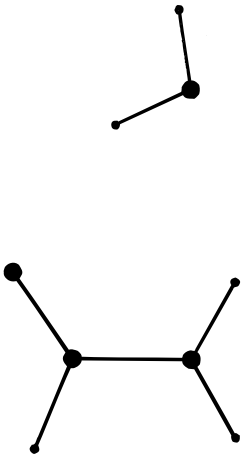

Figure 9. First structure of the formamide−water complex. This structure is the one in the global energy minimum.

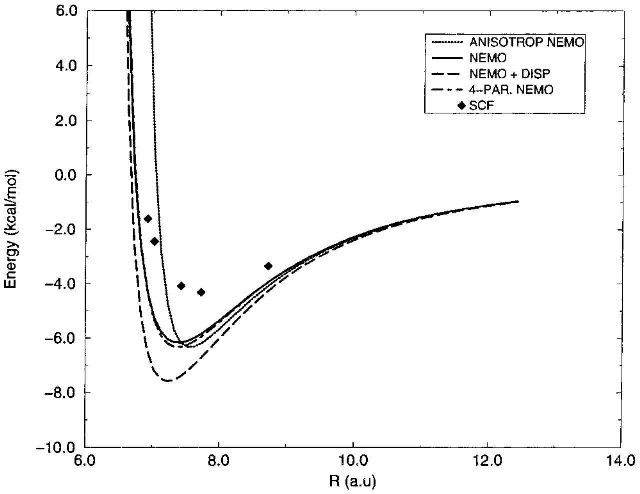

Figure 10. Interaction energy of the formamide−water complex as a function of the distance between the center of masses for structure II.

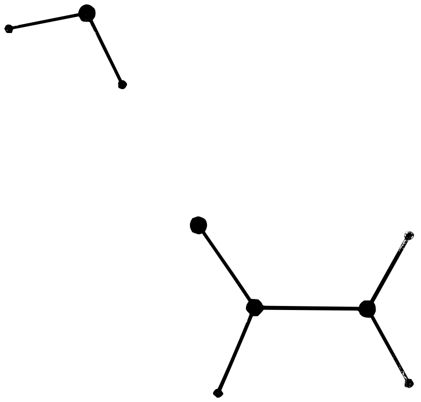

Figure 11. Second minimum structure of the formamide−water complex.

TABLE 8: Geometries and Energies (kcal/mol) for the Formamide−Water Complex at the Second Energy Minimum with Anisotropic and Isotropic Polarizabilities and Compared to Earlier Work

	this work		Engdahl[17]	
	aniso par[a]	iso par[b]	early model[e]	new model[f]
$R(O_F{-}H_w)$ (Å)[c]	1.94	1.94	1.83	1.83
$R(O_F{-}H_w)$ (Å)[d]	1.99	1.99		1.90
E_{int}	−8.59	−7.40	−6.00	−6.89
E_{ele}	−8.32	−8.32	−8.29	−8.87
E_{ind}	−2.23	−1.19	−2.11	−1.49
E_{rep}	4.38	3.35	6.59	5.01
E_{disp}	−2.41	−1.23	−2.19	−1.54

[a] Repulsion parameters from model 4′ in Table 1. [b] Repulsion parameters from model 5 in Table 1. This minima is not found with these parameters. [c] Distance between the atomic centers on the atoms. [d] Distance between the charge centers on the atoms. [e] Early model refers to work the done by Engdahl.[17] [f] Geometry used by Engdahl[17] but with the present NEMO model and repulsion parameters from model 5 in Table 1.

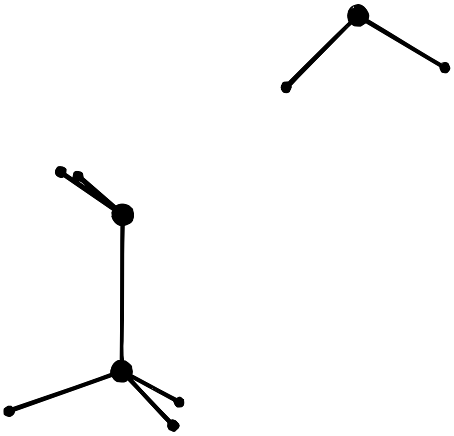

Figure 12. Structure of the methylamine−water complex in the potential minimum.

gave two geometries which are close in energy, minimum I in Figure 9 and minimum II in Figure 11 when we used the repulsion parameters from model 4′ in Table 1, but when we used the repulsion parameters from model 5 in Table 1 we could not find the second minimum in Figure 11. For minimum I, which we believe is the global minimum and which has been confirmed by others,[17,30] the agreement between the NEMO energies and the SCF points is very good. However, for minimum II in Figure 10, the SCF energies differ compared to ANISOTROP NEMO and NEMO. The energy difference between the SCF energy and the different potential curves in the potential minimum is about 2 kcal/mol which does not reflect the behavior of the other complexes at all. If we compare the energy contributions from our model with the old NEMO model[17] in Table 8, we see that we lack about 2 kcal/mol in the exchange repulsion energy. This corresponds to the difference between the NEMO energy and the SCF energy in the potential minimum. All other energy contributions are more or less the same. Obviously the new NEMO models give too little repulsion for this configuration. The only explanation we can find is that we have an unfortunate calcellation of errors in the different energy contributions for this geometry and that this errors adds up with the wrong sign. If the polarizabilities are made isotropic, minimum II is no longer a minimum but the interaction energy improves. Note that we do not know if minimum II is a minimum at the SCF or correlated level. This behavior shows that there is more work to do in how to model the polarizability on the atoms. The energy and geometry for the global minimum (minimum I) without the short-range parameters in Table 3 and with repulsion parameters from model 5 in Table 1 are $E_{int} = -9.61$ kcal/mol, $R_{O_F-H_w} = 1.88$ Å, and $R_{O_w-H_F} = 2.22$ Å. The distances are between the atomic centers. These numbers should be compared with the corresponding ones in Table 7, where we also make a comparison with the old NEMO model.

We note the same relation between the four-parameter model potential and the other NEMO potentials as in the other test

TABLE 9: Energies (kcal/mol) and Structures for Methylamine in Complex with Water and Ammonia in Their Respective Energy Minima

	methylamine−water			methylamine−ammonia	
	aniso par[a]	iso par[b]	Wee[30]	aniso par[a]	iso par[b]
$R(N_M-O_W)$ (Å)[c]	2.91	2.96	2.93		
$R(N_M-O_W)$ (Å)[d]	2.88	2.92			
$R(N_M-O_H)$ (Å)[c]	1.96	2.01		2.31	2.39
$R(N_M-O_H)$ (Å)[d]	2.00	2.05		2.37	2.44
E_{int}	−6.63	−6.24	−8.67	−3.02	−2.67
E_{ele}	−9.54	−8.91		−4.25	−4.04
E_{ind}	−1.89	−1.14		−0.63	−0.25
E_{rep}	6.56	5.01		2.90	2.61
E_{disp}	−1.75	−1.20		−1.04	−0.99

[a] Repulsion parameters from model 4′ in Table 1. [b] Repulsion parameters from model 5 in Table 1. [c] Distances between the atomic centers on the atoms. [d] Distances between the charge centers on the atoms.

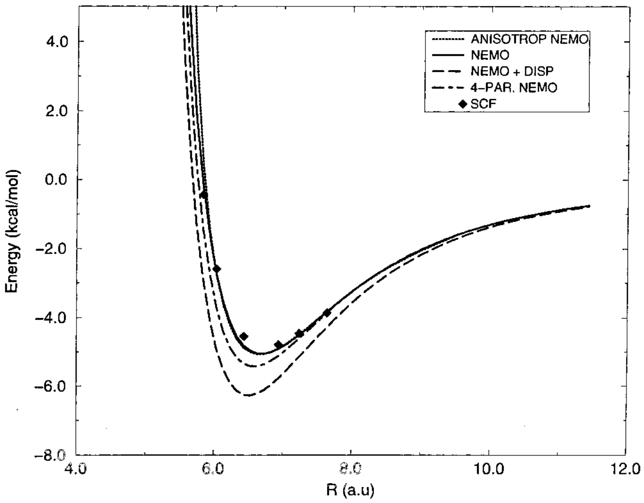

Figure 13. Interaction energy of the methylamine−water complex, as a function of the distance between the center of masses.

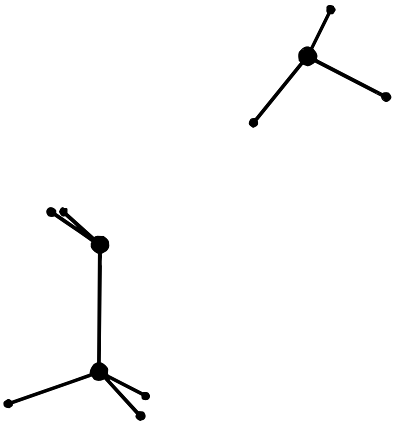

Figure 14. Structure of methylamine and ammonia in the potential energy minima.

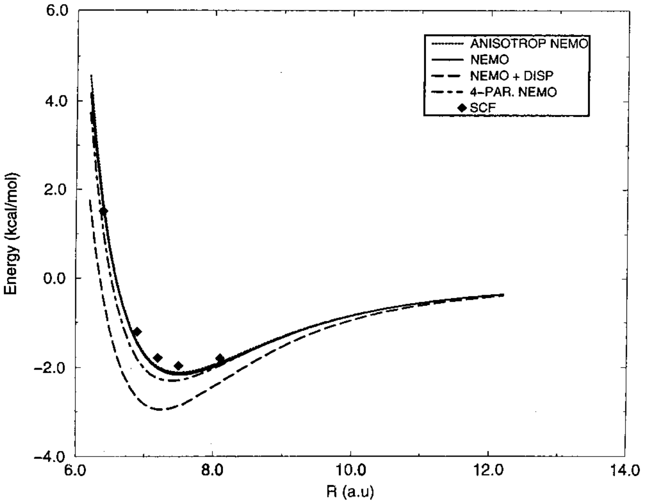

Figure 15. Interaction energy of methylamine−water complex as a function of the distance between the center of masses.

calculations. No comparison with SCF calculations was done in the earlier NEMO calculation.[17]

Methylamine−Water/Methylamine−Ammonia. Amines are organic derivatives of ammonia (NH_3). They are the most important compounds of organic chemistry that behave as bases where the amino group $-NH_2$ provides the characteristic basicity. The simplest amine is methylamine which is a prototype of side chain of proteins.

The structure for methylamine is taken from the report of Iijima *et al.*[31] We get the same hydrogen-bonding structure in the energy minimum for the methylamine−water complex (Table 9) as Wee *et al.*[30] do with a 6-31G basis set, but with some different energy. Wee *et al.*[30] make no correction for the BSSE which can explain the difference in interaction energy. A correction will make the attraction smaller and today there exist strong arguments for the BSSE corrections.[21,32,33] Correction for BSSE should be done for dimer complexes with smaller basis set. We also note that there is a fairly good agreement between the reduced four-parameter potential and the NEMO potential in Figure 13 and Figure 15. This good agreement with the SCF energies is promising for the general usage of the present model.

IV. Summary

In this study we have shown that it is possible to model the exchange repulsion between molecules containing small atoms (H−O) using information obtained from SCF Hartree−Fock calculations on the individual molecules. In particular, we note that the trace of the local electronic second moment tensor contains information about the size of the atoms and that the exchange repulsion depends on the number of valence electrons on the interacting atoms. We have also seen that the choice of expansion center and the electrostatic description used for modeling and definition of the exchange repulsion is important in the modeling. The number of parameters needed in the repulsion model is small, two for each type of atom. In the simplest model, thus, only four parameters are needed to describe the repulsion on the H, C, N, and O atoms, two for H and two for C, N, and O.

In this work, we have also investigated different models to describe the induction interaction. Here we have found that isotropic polarizability gives a slightly better fit than anisoptropic ones, and that for the small molecules studied in this work, polarizabilities obtained with local orbitals give a slightly poorer fit than polarizabilities obtained with canonical orbitals. In particular, we note that the modeling of the induction interaction is quite crucial for the description of the exchange repulsion, probably due to the short-range nature of these two types of interaction.

The different potential models have been tested on a series of complexes, some of which were in the original complexes used for the parametrization, and some new ones. The general trends are that the potentials used reproduce the results from quantum chemical calculations well, or very well. The perhaps most interesting result is that with the used functional form it is possible to model the exchange repulsion between molecules containing the atoms H, C, N, and O with only four parameters.

References and Notes

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