**Ab initio** calculation of the first order interaction energy in excited dimers. The H$_2$O–H$_2$O and H$_2$O–Ne dimers

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In order to interpret the solvation blue shift in the 'A$_1$→'B$_1$' UV band in H$_2$O (observed in liquid water, ice, and H$_2$O embedded in rare gas matrices) we have made ab initio calculations of the first order electrostatic and exchange interaction energies in H$_2$O*–H$_2$O and H$_2$O*–Ne dimers, after extending the usual symmetry adapted perturbation expressions to excited state molecules. We have found this shift to be caused mainly by the enlarged exchange repulsion between the excited H$_2$O molecule and its neighbors, originating from the extended (Rydberg) character of the excited 'B$_1$' state. The orientational dependence of this exchange repulsion has been calculated and correlated with the spatial distribution of the Rydberg state. The transition-dipole resonance interaction was found to be of little importance. These results were confirmed by supermolecule MO calculations on the ground state and excited dimers which showed moreover, an enlarged polarization of the excited H$_2$O (compared with the ground state), as well as some other effects that may be artifacts from the supermolecule treatment of excited dimers.

I. INTRODUCTION

The interaction energy of a molecule with its surroundings depends strongly on the electronic state of the molecule considered. This dependence can be observed as the different solvent shifts in the electronic absorption spectrum for different excited states of one and the same molecule. Both the intensity and the frequency shift aspects have been studied in numerous experiments. In some cases it has been found that a model where the interaction between solute and solvent molecules is described with the help of the multipole expansion for the electrostatic part, retaining only the dipole–dipole term, and a second order contribution represented by isotropic polarizability terms, explains the experimental results quite well. From later work it has become clear, however, that even relatively weak interactions between molecules at distances that occur in condensed phases, while all these molecules are in their electronic ground states, generally cannot be described using only (truncated) multipole expansions. This is a direct consequence of the occurrence of charge overlap leading to the breakdown of the multipole expansion on the one hand and to the so-called exchange repulsion on the other. Therefore any approach that tries to explain the solvent shift and confines itself to changes in multipole interaction terms is liable to fail, as is frequently observed in practice.

As a first step towards a more complete treatment we consider in this article the detailed first order perturbation treatment of the interaction between molecules in ground and excited state. Taking a testcase of practical interest, we study water–water and neon–water dimers.

Although no common solvents are available where the solvent shift for the water molecule can be observed, there is ample related information available, when we confine ourselves to the lowest excited singlet state. The gas phase spectrum is known over 50 years and well-understood. The spectrum of the pure liquid, which can be considered as the spectrum of a water molecule when dissolved in water, has been measured in different ways ten years ago. Although the results of different authors do not completely agree, information is available for ice as a function of temperature. Finally we have measured the spectrum of H$_2$O in an argon matrix at 15 K at a variety of concentrations, including those where water–water interactions can be neglected. The system then has close analogy to a dilute solution of polar molecules in an apolar solvent. The experimental data are collected in Fig. 1.

From this figure it becomes clear that there is a systematic 1 eV blue shift when going from the gas phase to the condensed phases. This value indicates a large difference in interaction energy for ground and excited state. Recent quantumchemical calculations indicate that the hydrogen bond energy for the water dimer in its most stable configuration in the ground state amounts to 5–6 kcal/mol (0.25 eV). When we assume that the solvent effect can be attributed mainly to dimer effects, the interaction in the excited state has to be 0.75 eV re-
pulsive. As is usual in the treatment of solvent effects we take the Franck-Condor principle for granted and consider only vertical excitation.

The solvent shift is seen to be rather independent of the nature of the neighbors (unordered solvent water molecules in the liquid, ordered water molecules in the solid, and argon atoms in the matrix). Therefore, one may assume that this large change is mainly related to the character of the excited state of the water molecule.

The gasphase spectrum as given in Fig. 1 is due to the \( 1B_1 \to 4A_1(3S_0) \) transition (in a one electron picture).

Though results of \( ab \) initio calculations for the vertical excitation to that state have been published earlier\(^\text{15,22} \) we have repeated the calculation using the SCF formalism for the monomer ground state and the electron hole potential (EHP) method of Morokuma et al.\(^\text{33,36} \) for the \( 1B_1 \) excited state. We investigated a small part of the monomer potential surface, relevant for the interpretation of the gasphase absorption spectrum.

The dimers were studied by exchange perturbation theory.\(^\text{24} \) This theory has been used until now mainly for the treatment of the interaction between ground state atoms and molecules. In the case of interacting closed shell systems a formalism using interaction density matrices was presented by Jezierski \textit{et al.} and applied to the \( He_b \) system.\(^\text{25} \) The same formalism was used later for the treatment of the water dimer.\(^\text{35} \) In the present article the formalism has been extended to include molecules described by singly excited states.

Numerical results of the application of this formalism to the water dimer in some relevant geometries are described. Moreover for the interpretation of the matrix isolation studies, calculations for the mixed neon-water dimers, replacing either donor or acceptor water by neon have been performed. Finally some direct SCF and EHP computations on the dimers have been performed also.

II. EXPRESSIONS FOR THE FIRST ORDER INTERACTION ENERGY

For a system consisting of two closed shell molecules, \( A \) and \( B \), the first order part of the interaction energy in exchange perturbation theory is given by

\[
E_{1\text{st}}^{(1)} = \frac{\langle \Phi_0 | V_{AB} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle},
\]

where \( \Phi_0 = \Psi_A \Psi_B \) is the simple product of the wave functions describing the free molecules, \( \alpha \) is the (idempotent) antisymmetrizer for all electrons in the system, and \( V_{AB} \) contains the Coulombic interaction between the electrons and nuclei of \( A \) on the one hand and those of molecule \( B \) on the other. When we adhere to the notation that \( \lambda, \mu \) stand for nuclei, \( i, j, k, l \) for electrons and \( p, q, r, s \) for spin orbitals, the interaction operator \( V_{AB} \) may be written as (in a.u.)

\[
V_{AB} = W_{AB} + \sum_i \sum_j V_{1A}(i) + \sum_j V_{1B}(j) + \sum_i \sum_j \frac{1}{r_{ij}},
\]

where

\[
W_{AB} = \sum_{\mu} \sum_{\nu} Z_{\mu} Z_{\nu} R_{\mu\nu},
\]

is the nuclear repulsion energy and

\[
V_{1A}(i) = \sum_{\mu \neq x} \frac{Z_{\mu}}{r_{\mu i}},
\]

is the potential energy of electron \( i \) in the electric field of the nuclei in molecule \( X \), \( Z_{\mu} \) are nuclear charges, and \( R_{\mu\nu}, r_{\mu i} \) are distances between nuclei and electrons indicated by the subscripts \( \mu, \nu, i, j \). In Ref. 27 it is shown how formula (1) can be evaluated for closed shell systems \( A \) and \( B \) using suitably defined interaction density matrices (IDM's). These IDM's differ from the usual first and second order (reduced) density matrices as for instance defined in Ref. 29, due to the fact that the function \( \Phi_0 \) is not antisymmetric in all its arguments.

When one of the molecules is in an excited state we meet degeneracy as soon as the molecules are identical. The degeneracy arises not necessarily from spatial symmetry. Even when there is no symmetry operation that transforms the molecular coordinates into each other, the zeroth order wave function denoted as \( \Phi_0^x \) can be given as

\[
\Phi_0^x = C_1 \Psi_A^x \Psi_B + C_2 \Psi_A \Psi_B^x,
\]

where the values of \( C_1 \) and \( C_2 \) have to be determined yet, using perturbation theory for degenerate states. Now we write the exact (perturbed) wave function for the excited dimer as

\[
\Phi^x = \Phi_0^x + \chi^x,
\]

where \( \chi^x \) is a correction function that contains all higher order contributions. We require this correction function to be orthogonal to all the degenerate zeroth order functions:

\[
\langle \Psi_A^x | \Psi_B | \chi^x \rangle = 0, \quad \langle \Psi_A | \Psi_B^x | \chi^x \rangle = 0.
\]

The Schrödinger equation for the perturbed system is

\[
(\mathcal{H}_0 - E_0^x + V_{AB} - E_{1\text{st}}^x)(\alpha \Phi_0^x + \chi^x) = 0
\]

with

\[
3C_0 = 3C_A + 3C_B
\]

and

\[
E_0^x = E_A^x + E_B - E_{1\text{st}}^x.
\]

In passing we may note that these expressions can easily be generalized to a system of many identical atoms or molecules where excitation occurs. When we indicate the degenerate excited configurations with a single wave function \( \alpha \), the zeroth order wavefunction can be written as

\[
\Phi_0^x = \sum_{\alpha} C_{\alpha} \alpha.
\]

Multiplying Eq. (8) from the left with each of the zeroth order functions \( \alpha \) and making a perturbation expansion, we obtain the equation for the coefficients \( C_{\alpha} \) and the first order contribution to the interaction energy \( E_{1\text{st}}^x \).

\[
\mathbf{VC} = E_{1\text{st}}^x \mathbf{SC}
\]

with
\[ V_{ab} = \langle \alpha \gamma \beta \delta \rangle \quad (13) \]
\[ S_{a\delta} = \langle \alpha \beta \gamma \delta \rangle . \quad (14) \]

Although at first sight the matrix \( V_{ab} \) appears not to be Hermitian this can still be proved, if the unperturbed wave functions are exact eigenfunctions of \( H_0 \). For approximate monomer wave functions (e.g., Hartree—Fock LCAO functions) as we encounter in practical calculations \( V \) is not Hermitian indeed. [Using real wave functions we never had the problem that the eigenvalues of Eq. (12) were complex, due to the deviations of \( V \) from being symmetric.]

Equation (12) is very similar to the well-known expression for the excitation energy in a molecular crystal according to the exciton formalism.\(^3\) The main difference is the omission of the antisymmetrizer from the (usual) exciton wave function. (Although sometimes introduced formally, the antisymmetrizer generally disappears at the time of actual calculation.) Therefore there is no problem with the hermicity of the matrix \( V \) in exciton theory. On the other hand, the exchange interactions are lacking; they may be implicitly taken into account when the theory is parametrized.

When the wave functions \( \alpha \) are described with the help of molecular orbitals of the different monomers, we have to take into account that orthogonality exists generally only between orbitals stemming from one and the same monomer. The elements of the \( V \) and \( S \) matrices, (13) and (14), can then be expressed most easily in terms of diagonal elements of first and second order transition interaction density matrices (TIDM’s) \( \gamma_1 \) and \( \gamma_2 \). In the case of a dimer we write

\[ V_{ab} = \int V_{1A}(k) d\gamma_1^{\text{up}}(\alpha \beta | x) dx_k + \int V_{1B}(l) d\gamma_1^{\text{up}}(\alpha \beta | x) dx_l \]
\[ + \int \gamma_2^{\text{up}}(\alpha \beta | x_i, x_i) \frac{1}{\gamma_1} dx_k dx_l . \quad (15) \]

The definition of \( \gamma_1 \) and \( \gamma_2 \) is

\[ \gamma_1^{\text{up}}(\alpha \beta | x) = N_A \int \alpha^* \alpha \beta \quad (16) \]

\[ \gamma_2^{\text{up}}(\alpha \beta | x_i, x_i) = N_A N_B \int \alpha^* \alpha \beta \quad (17) \]

\( k \) and \( l \) are electrons belonging to the molecules \( A \) and \( B \), respectively. \( N_A \) is the number of electrons in molecule \( X \) (\( X \) is \( A \) or \( B \) ). \( \gamma_k \) means integration over all electron coordinates \( x_k \) except those of electron \( k \). Similarly \( \gamma_1 \) excludes \( x_k \) from the integration.

The main difference between the TIDM’s from (16) and (17) and the IDM’s in Ref. 27 is of course the occurrence of \( \alpha \) and \( \beta \). Since an excited state can in general not be well-described with one determinant constructed from doubly occupied molecular orbitals, in the evaluation of the TIDM’s one has to take the occurrence of open shells into account.

When we have chosen to describe the ground state with a SCF wave function three methods are available to produce wave functions for the excited state on a nearly equal level of sophistication. Of these methods the open shell restricted Hartree—Fock approach has the disadvantage that it produces sets of molecular orbitals for ground and excited states that are not all orthogonal among each other (unless by symmetry). The full singly excited state configuration interaction method has the drawback of many expansion coefficients and the need of a computer time consuming integral transformation. We found that an only slightly inferior wave function is produced by the EHP method\(^23–25\) lacking the drawbacks of the two other methods. The EHP method uses a one configuration function for a singly excited state, so in the case of a singulet (with no orbital degeneracy) this wave function consists of two determinants built from a set of orthogonal molecular orbitals. One orbital in the set, which contains the excited electron, is a linear combination of the virtual (ground state) SCF orbitals, the remaining orbitals are produced by a unitary transformation of the occupied ground state SCF MO’s. (The same unitary transformation may be applied to the ground state wave function without affecting the ground state properties.) The transformation matrices are determined by the requirement of minimal excitation energy.

The evaluation of the matrix elements of (13) and (14) using SCF and EHP functions is described in Appendix A. We may note that the resulting expressions for \( \gamma_1 \) and \( \gamma_2 \) can also be used in those cases where the excited state functions are given by linear combinations of singly excited configurations. Only computer time is a limiting factor.

When we neglect all antisymmetrizers specified in (13) and (14) we arrive at the expression for the electrostatic contribution to the interaction energy. Of course also the mixing coefficients will change in general. The so-called exchange contribution is found as the difference between the total first order energy resulting from the solution of (12) and the electrostatic contribution.

III. NUMERICAL EVALUATION

A. Properties of excited H\(_2\)O

From previous calculations of the excited states of the water molecule\(^16–22\) it has become clear that for a reasonable description of the excited \( ^1B_1 \) (Rydberg state) the basis set must at least contain relatively diffuse 3s type atomic orbitals on the oxygen atom. To keep the basis set balanced we also included 3p functions on oxygen and 2s and 2p functions on hydrogen. Exponents were derived from Slater’s rules and converted to a single Gaussian. The \( \alpha \) values so obtained (O 3s: 0.018, 3p: 0.031; H 2s: 0.025, 2p: 0.038) do not differ much from Dunning’s\(^31\) suggested values. To avoid long computation times we used a modest basis set for the inner shell and valence shell electrons, taken from Clementi and Mehl.\(^32\)

With this basis set the energy of the ground state and the \( ^1B_1 \) excited state was computed at a small part of the potential surface, namely: varying one O–H distance and the HOH angle, keeping the other OH distance fixed at 1. 80888 a. u. This part was chosen in accordance with the accepted interpretation of the observed gas
Values of some computed properties, both in the ground and in the excited state are collected in Table I. The components of the polarizability tensor have been computed by the finite field approach, applied to the SCF and EHP formalisms. The values have been derived from the change in dipole moment upon application of an electric field of strength 0.005 a.u. along each of the x, y, or z axes. The value of the polarizability in the excited state is much larger than in the ground state. Also the anisotropy is greater in the excited state. Part of the anisotropy in the ground state is certainly due to the lack of d functions in the basis set. At the present time it seems impossible to verify by electro-optical experiments the enormous increase in polarizability upon excitation. These properties will be used in a later section. For completeness the vertical excitation energy for some higher states has been computed as well. Results are given in Table II.

**Table I.** Properties of the H\textsubscript{2}O monomer computed from SCF (ground state) and EHP(\textit{2}B\textsubscript{1} excited state\textsuperscript{*}) wave functions. Molecule in \textit{yz} plane, \textit{C}_{2} axis along \textit{z} axis, \textit{O} largest \textit{z} coordinate. All quantities are in atomic units.

<table>
<thead>
<tr>
<th>Property</th>
<th>\textit{(\mu)}</th>
<th>\textit{(\mu^{*})}</th>
<th>\textit{(Q)}</th>
<th>\textit{(Q^{*})}</th>
<th>\textit{(O)}</th>
<th>\textit{(O^{*})}</th>
<th>\textit{(q)}</th>
<th>\textit{(q^{*})}</th>
<th>\textit{(\langle r^{2}\rangle)}</th>
<th>\textit{(\langle r^{2}\rangle^{*})}</th>
<th>\textit{(\alpha)}</th>
<th>\textit{(\alpha^{*})}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>(-1.02)</td>
<td>(+0.92)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(-1.03\ -1.84\ 0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
<td>(+1.77\ -1.84\ -0.07)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In parentheses best SCF results.

\textsuperscript{b}Reference 51.

\textsuperscript{c}Reference 40.

\textsuperscript{d}Reference 19.

Of course the contributions of the zero point vibrational energy in the ground state (\(-0.6\) eV) and the possibility of excited vibrational modes in the electronic excited state have to be taken into account. The latter being unknown, the agreement could be fortuitous. Nevertheless we think that our wave function represents both ground and excited state sufficiently well to be used as a basis for the dimer calculations. The inclusion of both 3\(s\), 3\(p\) orbitals on oxygen and 2\(s\), 2\(p\) orbitals on hydrogen is justified, since their omission would lead to a much (1 eV) higher excitation energy. This is of course due to the Rydberg character of the excited \(2\text{B}\textsubscript{1}\) state.

McGlynn and co-workers have recently observed some structure superimposed on the absorption continuum. This was interpreted as being caused by transitions to higher vibrational levels of the bending vibration in the excited state. The vibrations in the excited state must be shifted to about \(-20\%\) higher frequencies with respect to the ground state value. This increase in bending force constant is not substantiated by our computed results. To settle this problem, calculations with larger basis sets and large CI are certainly needed. Our ground state equilibrium angle is somewhat too large, which is not uncommon in limited basis set calculations (in fact, computed values between 100 and 115 deg have been published\cite{36,38}). The vertical excitation energy at the equilibrium geometry (0.313 a.u. \(-8.5\) eV) coincides reasonably well with the energy associated with the position of the maximum in the absorption band at 1650 \(\AA\) (7.5 eV) observed in the gasphase and with the results of more elaborate calculations.\cite{16,22}. Of course the computed potential surface for the water molecule in the lowest \('A'\ and \('A''\) states. (a) the \(OH\) distance is varied, the \(OH\) and \(H\) bond angles are kept at their experimental equilibrium values. (b) the \(H\) bond angle is varied for different values of the \(OH\) distance and constant (experimental) \(OH\) distance. Energies and distances in a.u.
TABLE II. Singlet excited states of H₂O. Vertical excitation energies (in a.u.), symmetries in C₆ and reduction in Cᵥ (the symmetry of the dimer in geometry I) for molecules A and B (see Fig. 3).

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Type</th>
<th>Symmetry C₆(A)</th>
<th>Symmetry Cᵥ(B)</th>
<th>Computed excitation energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂ᵥ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₁</td>
<td>1b₁₋₋₄a₂(ν₋₋₃s)</td>
<td>A''</td>
<td>A''</td>
<td>0.314</td>
</tr>
<tr>
<td>A₂</td>
<td>1b₁₋₋₂b₁(ν₋₋₃pₓ)</td>
<td>A''</td>
<td>A'''</td>
<td>0.378</td>
</tr>
<tr>
<td>A₁</td>
<td>3a₁₋₋₄a₁</td>
<td>A'</td>
<td>A'</td>
<td>0.393</td>
</tr>
<tr>
<td>A₁</td>
<td>1b₁₋₋₂b₁(ν₋₋₃pₓ)</td>
<td>A'</td>
<td>A'</td>
<td>0.434</td>
</tr>
<tr>
<td>B₂</td>
<td>3a₁₋₋₂b₁</td>
<td>A'''</td>
<td>A'</td>
<td>0.420</td>
</tr>
<tr>
<td>B₁</td>
<td>3a₁₋₋₂b₁</td>
<td>A'''</td>
<td>A'</td>
<td>0.420</td>
</tr>
<tr>
<td>A₂</td>
<td>1b₂₋₋₂b₂</td>
<td>A''</td>
<td>A''</td>
<td>0.528</td>
</tr>
<tr>
<td>A₁</td>
<td>1b₂₋₋₂b₂</td>
<td>A''</td>
<td>A''</td>
<td>0.621</td>
</tr>
<tr>
<td>A₁</td>
<td>1b₂₋₋₂b₁</td>
<td>A''</td>
<td>A''</td>
<td>0.626</td>
</tr>
</tbody>
</table>

The missing 1b₁₋₋₅a₁(ν₋₋₃pₓ) transition found at 0.370 a.u. in the CI calculations of Ref. 22, cannot be obtained with the EHP method, since it is not the lowest of its excitation type.

B. Dimer calculations

The numerical evaluation of formula (13) according to the expressions given in the appendix is straightforward once the one- and two-electron integrals over molecular orbitals are available. For this purpose the general N⁴ four index transformation program used in previous studies²⁶,²⁷ has been modified in order to produce the about 2m² two-electron molecular orbital integrals needed in the most efficient way avoiding all multiplications with zero vector components (m equals the total number of molecular orbitals used for the description of the excited multimer, so in the case of the water dimer m = 12). The computation of the inverses and determinants of the symmetric and asymmetric overlap matrices was executed with the help of NAG library routines.⁴¹

In the supermolecule approach the definition of binding energy for a complex AB in some specified state at distance R is given as

\[ E_{\text{ss}}(AB,R) = E(AB,R) - E(A) - E(B) \]

where \( E(AB,R) \) is the energy of the complex AB at distance \( R \) and \( E(A) \) and \( E(B) \) are the energies of the dissociation products of AB. When we incorporate the correction for the basis set superposition error according to the counterpoise method,⁴² this expression becomes on the SCF level

\[ E_{\text{ss,SCF}}(AB,R) = E_{\text{SCF}}(AB,R) - E_{\text{SCF}}(A,R) - E_{\text{SCF}}(B,R) \]

where \( E_{\text{SCF}}(AB,R) \) is the SCF energy of AB at distance \( R \) and \( E_{\text{SCF}}(A,R) \) is the SCF energy obtained for A in the basis set of the complex at distance \( R \) and analogously for \( E_{\text{SCF}}(B,R) \).

We can give a similar definition for the binding energy in the excited dimer at the EHP level

\[ E_{\text{ss,EHP}}(A^{**}B,R) = E_{\text{EHP}}(A^{**}B,R) - E_{\text{EHP}}(A^{**},R) - E_{\text{EHP}}(B,R) \]

Here \( E_{\text{EHP}}(A^{**}B,R) \) is the energy obtained by the EHP formality for the excited dimer with excitation mainly localized on A and \( E_{\text{EHP}}(A^{**},R) \) is the energy of excited A when computed in the basis set for AB at distance \( R \).

Now the excited state energies in the EHP formalism are found as the sum of the SCF ground state energy and the variationally minimized excitation energy \( \Delta E_{\text{EHP}} \)

\[ E_{\text{EHP}}(A^{**}B,R) = E_{\text{SCF}}(AB,R) + \Delta E_{\text{EHP}}(A^{**}B,R) \]

and

\[ E_{\text{EHP}}(A^{**},R) = E_{\text{SCF}}(A,R) + \Delta E_{\text{EHP}}(A^{**},R) \]

where again \( \Delta E_{\text{EHP}}(A^{**},R) \) is the excitation energy found for the monomer A using the dimer basis set. Substituting (21) and (22) into (20) we obtain:

\[ E_{\text{ss,EHP}}(A^{**}B,R) = E_{\text{ss,SCF}}(AB,R) + \Delta E_{\text{EHP}}(A^{**}B,R) - \Delta E_{\text{EHP}}(A^{**},R) \]

It must be pointed out however, that the counterpoise method used both for the ground state and for the excited state has been justified, both theoretically⁴² and numerically⁴³ for the ground state only. In the excited state extra complications may arise. The excitation on one of the monomers may change its character or become delocalized due to the presence of the neighbor. In the latter case we must also keep in mind that the asymptotic behavior of the dimer SCF and EHP wave function for \( R \to \infty \) may be incorrect. The results of excited dimer supermolecule calculations must therefore be interpreted with great care.

In practice we used the same set of computer programs as for the water monomer calculations. In the EHP method we used the occupied SCF orbitals for the ground state dimer and one appropriate virtual orbital as starting vectors for the orbitals of the excited state.

IV. RESULTS OF H₂O-H₂O DIMER CALCULATIONS

For two sets of geometries the complete first order interaction energy and its components have been evaluated. In the first set, in the following referred to as geometry I, the effect of a change in intermolecular dis-
FIG. 3. Mutual orientation of the two water molecules considered. In geometry I only the O···O distance is varied. In geometry II the O···O distance is kept constant at 5.67 a. u. and the plane of molecule A is rotated around the O···O axis. Exact values for the coordinates in geometry I can be found in Ref. 28.

distance at a fixed angular orientation is considered (Fig. 3). For the ground state this geometry had been studied previously using extensive basis sets.\textsuperscript{28} This gives us the opportunity to investigate the existence of a hydrogen bond in the excited dimer. Moreover we have a means of observing the basis set effects in the ground state. In Table III and Fig. 4 the results of our calculations are shown. Due to the fact that the zeroth order wave functions \(\psi_A\) and \(\psi_B\) belong to different irreducible representations (\(A'\) and \(A''\) in \(C_s\), the symmetry group of the dimer in geometry I), no off-diagonal \(V\) and \(S\) matrix elements arise. In this case the diagonal elements of the interaction operator for the two (normalized) zeroth order wave functions directly give the interaction energies in the two possible states.

At large intermolecular distance (12 a. u.) the exchange contributions are negligibly small and the interaction energy is determined by the electrostatic contribution. This is the case, both for the ground state and for the two excited states. In the ground state the electrostatic contribution is attractive, in the two excited states repulsive. This can be easily understood since at this distance the electrostatic interaction is determined largely by the first nonvanishing term in the multipole expansion,\textsuperscript{46} i.e., the dipole–dipole term for the water dimer. In the first excited state of the monomer the dipole moment has about the same absolute value as in the ground state, but its direction is reversed, as can be seen in Table I. The results of the multipole expansion compared with the unexpanded results are listed in Table IV.

At intermediate and shorter distances (<9 a. u.) we observe that the exchange repulsion in both excited configurations increases much faster when the molecules approach than it does in the ground state. This increase in exchange repulsion is most striking for the A\(^{ex}\)B configuration. Clearly the \(1B_1\) Rydberg state is not spherically symmetric. The charge distribution must have a rather pronounced extension along the direction of the O–H bonds. Also for the electrostatic part the pene-

TABLE III. Total first order and electrostatic interaction energy for two water molecules (geometry I).

<table>
<thead>
<tr>
<th>State</th>
<th>AB</th>
<th>A(^{ex})B</th>
<th>AB(^{ex})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{\text{rep}}/d_0)</td>
<td>(R_{\text{rep}}/\text{Å})</td>
<td>(E_{\text{Tot}})</td>
<td>(E_{\text{Elst}})</td>
</tr>
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<td>7690(12 815)</td>
<td>–35 527(– 27 198)</td>
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<td>–4757 (1468)</td>
<td>–23 224 (–17 098)</td>
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<td>–8015 (–3541)</td>
<td>–15 160 (–11 046)</td>
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<td>–6363 (–4455)</td>
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<td>–2630 (–1782)</td>
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<td>6.35</td>
<td>–1015</td>
<td>–1017</td>
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TABLE IV. Cumulative contribution of the multipole series terms and total unexpanded electrostatic energy. Energies in 10^{-6} a.u.

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<th>State</th>
<th>( \phi )</th>
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<th>( E(AB)_{elst} )</th>
<th>( E(AB)^{2} )</th>
<th>( V_{12} )</th>
<th>( V_{21} )</th>
<th>( S_{12} \times 10^{6} )</th>
<th>( E_{I} )</th>
<th>( C_{I,1} )</th>
<th>( C_{I,2} )</th>
<th>( E_{II} )</th>
<th>( C_{II,1} )</th>
<th>( C_{II,2} )</th>
</tr>
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<td>10234</td>
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<td>0</td>
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<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
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<td>10260</td>
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<td>1677</td>
<td>2183</td>
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<td>11711</td>
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<td>8510</td>
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<td>0.733</td>
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<td>2243</td>
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<td>7595</td>
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<tr>
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<tr>
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<td>8447</td>
<td>0.0</td>
<td>1.0</td>
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Next we consider (in geometry II) the effect of rotation of monomer A around the O-O axis keeping the O-O distance fixed at 5.67 a.u. (the equilibrium distance for the ground state). Rotations of 60 and 180 deg produce the nearest neighbor orientations that are present in hexagonal ice but not in cubic ice. A rotation of 120 deg produces the other orientation possible in both cubic and hexagonal ice. In all these rotated dimers (except for the 180 deg one) no symmetry element remains and the off-diagonal S and V matrix elements will be nonzero. In Table V.A the diagonal and off-diagonal matrix elements and the resulting eigenvectors and eigenvalues are given as a function of rotation angle. In Table V.B the same is done taking only the electrostatic contribution into account. The great difference between electrostatic and total first order results shows that the "resonance dipole contribution" normally responsible for the first order energy is completely overshadowed by exchange effects. This can be understood because the diffuseness of the Rydberg excited state leads to a large exchange repulsion between the molecules already at large distances, while, on the other hand, the transition moments which determine the dipole resonance energy are generally small for Rydberg states (computed from our EEP wave function 0.46 a.u., experimentally 0.6 a.u.).

The computed value of 0.46 a.u. leads to a value for the dipole-dipole term in the off-diagonal element of the electrostatic part of the interaction operator of 1.1 \times 10^{-3} a.u. for the dimer with 90° rotation and 5.67 a.u. interoxygen distance. This value is somewhat larger.

TABLE V. A. Total first order interaction energy for two water molecules as a function of orientation at fixed distance (geometry II). Energies in 10^{-6} a.u.

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<tr>
<th>( \phi )</th>
<th>( E(AB) )</th>
<th>( E(AB)_{elst} )</th>
<th>( E(AB)^{2} )</th>
<th>( V_{12} )</th>
<th>( V_{21} )</th>
<th>( S_{12} \times 10^{6} )</th>
<th>( E_{I} )</th>
<th>( C_{I,1} )</th>
<th>( C_{I,2} )</th>
<th>( E_{II} )</th>
<th>( C_{II,1} )</th>
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<td>-27706</td>
<td>934</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-27706</td>
<td>1.0</td>
<td>0.0</td>
<td>934</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
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<td>-28116</td>
<td>959</td>
<td>373</td>
<td>29138</td>
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<td>0.999</td>
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<td>0</td>
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<td>0.963</td>
<td>0.013</td>
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<tr>
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<tr>
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<td>30968</td>
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<tr>
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<td>382</td>
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<td>1110</td>
<td>0.0</td>
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TABLE V. B. Electrostatic contribution to the first order interaction energy.

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<th>( E(AB)_{elst} )</th>
<th>( V_{12} )</th>
<th>( V_{21} )</th>
<th>( S_{12} \times 10^{6} )</th>
<th>( E_{I} )</th>
<th>( C_{I,1} )</th>
<th>( C_{I,2} )</th>
<th>( E_{II} )</th>
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<td>-27706</td>
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<td>0</td>
<td>0</td>
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<td>1.0</td>
<td>0.0</td>
<td>934</td>
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<tr>
<td>30</td>
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<td>-28116</td>
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<td>0.022</td>
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<td>0</td>
<td>0</td>
<td>31546</td>
<td>1.0</td>
<td>0.0</td>
<td>1110</td>
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M. van Hemert and A. van der Avoird: Interaction energy in excited dimers

FIG. 5. First order interaction energy for the water dimer in ground (AB) and excited (I and II) states according to exchange perturbation theory for degenerate states for geometry n. The values of the diagonal elements of the interaction operator are indicated by 1: A"B and 2 :ABex. Also given are the values of the overlap matrix S for the (normalized) degenerate state functions and the off-diagonal elements V12 and V21. Abscissa: rotation angle (deg) of the plane of molecule B around the O···O axis (cf. Fig. 3).

In Fig. 5 we see that the A"B and ABex energy curves cross. The energy of the ABex state is nearly independent of the rotation angle, while the A"B state energy is not. The crossing is avoided by taking the off-diagonal elements into account. The correct zeroth order wave function for the lowest excited state of the dimer changes smoothly from ABex at 0° to A"B at 180°. The behavior of the coefficients is shown in Table V.A.

V. RESULTS FOR THE WATER NEON DIMER

In order to gain more insight in the origin of the results mentioned above and as an aid for the interpretation of the matrix isolation studies we have repeated the dimer calculations with either the A or the B water molecule replaced by the isoelectronic Ne atom. We have considered only the A"Ne and NeBex zeroth order configurations. As a basis set for neon we used the uncontracted 9s 5p set from Huzinaga. Values of the first order interaction energy are given in Table VI and represented graphically in Fig. 6.

In the ground state we see of course that the electrostatic interactions are greatly reduced for both Ne-H2O dimers when compared with the H2O-H2O dimer, which can be expected from the combined effect of the absence of permanent multipole moments on neon and the smaller van der Waals radius (yielding less charge penetration). The decrease is largest for Ne-H2O, probably due to the fact that the presence of the H atoms on the O-Ne axis in the H2O-Ne dimer is responsible for an earlier onset of penetration effects. The exchange part follows the same pattern with opposite sign. In the excited state the situation is more complicated. For the H2O-Ne dimer the interaction curves are shifted about 2 a.u. outwards when compared with the ground state while for the Ne-H2O dimer this shift is only 0.5 a.u. This seems to stress the importance of the extension of the Rydberg molecular orbital towards the H atoms. It is confirmed

![Graph](https://via.placeholder.com/150)

**TABLE VI.** First order interaction energy for the water—neon and neon—water dimers. Distances in a. u., energies in $10^{-6}$ a. u.

<table>
<thead>
<tr>
<th>R0AB, a. u.</th>
<th>ETot (A Ne)</th>
<th>Eelst (A Ne)</th>
<th>ETot (A&quot;Ne)</th>
<th>Eelst (A&quot;Ne)</th>
</tr>
</thead>
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<td>35.193</td>
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<td>71.4</td>
<td>-95.9</td>
</tr>
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<td>R0Ne-Ob, a. u.</td>
<td>ETot (Ne B)</td>
<td>Eelst (Ne B)</td>
<td>ETot (NeBex)</td>
<td>Eelst (NeBex)</td>
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<tr>
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<td>-15</td>
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</table>

FIG. 6. First order interaction energy for water—neon dimers in ground (NeB and ANe) and excited (NeBex and A"Ne) states. Full line: according to exchange perturbation theory, dashed line: only electrostatic contributions taken into account.
by a Mulliken population analysis (Table II). We have to conclude that a change from slightly positive charge on H to a negative value on the same atom, accompanied by an opposite change in oxygen charge can well-explain a great deal of our results. Moreover we have always to consider the increase in size of the charge cloud upon excitation.

VI. RESULTS OF SUPERMOLECULE CALCULATIONS

In addition to the first order perturbation theory calculations we have also performed supermolecule SCF and EHP calculations for the H$_2$O-H$_2$O (geometry I only) and H$_2$O-Ne dimers, since dimer SCF and EHP calculations can be expected to include more different physical effects, in particular induction. On the other hand the problem of the basis set superposition error arises. In the EHP method, as in SCF, basis set effects can play an important role when the method is applied to dimers, as can be seen in Ref. 25. We have therefore corrected the excited state binding energies found with the EHP method in the same way as the ground state binding energies, although some uncertainty regarding the applicability of the counterpoise method to excited state problems exists (see Sec. III B).

In geometry I there is no need for the use of multicomponent EHP methods. We have found that both for the mainly A$^+$B excited state with $A''$ symmetry and the AB$^{**}$ state with $A'$ symmetry no other low lying excited state of the same symmetry could be generated. Results of the SCF and EHP computations are given in Table VII and Fig. 7. For the ground state we find a somewhat too low minimum which is too far inward. This is common in calculations without very large basis sets, even when the counterpoise procedure is used. (Generally all multipole moments are computed with a too high value and the charge distribution is too compact leading to an overestimate of the electrostatic attraction on the one hand and too small exchange repulsion on the other). Furthermore a comparison of the SCF and first order results learns that the induction contribution must be somewhat too small also. This is due to a lack of appropriate polarization functions in the basis set.

In the excited state we find at long range (12 a.u.) for both configurations a repulsion that is smaller than the one found in the first order calculations. Again by subtraction of the first order energy the induction part can be obtained (at least when we assume that in the EHP method just as in supermolecule SCF no other contributions to the binding energy are important). This induction energy has a much larger value than in the ground state, in accordance with our result from finite field calculations that the computed excited state polarization is about ten times larger than the ground state value (see Table I).

At intermediate and shorter distances the picture is unexpected, at least for the mainly A$^+$B state. In the EHP excited state molecular orbital we find an extra large coefficient for the diffuse s orbital on the H atom on the O⋯O axis. This coefficient points to a large contribution from the excitation which, at infinite distance, leads to the $1^A_g$ excited state for the A molecule. According to symmetry this is possible since for the A molecule both $1^B_1$ and $1^A_2$ states reduce to a $1^A''$ state in the dimer. For the excitation localized on the B molecule such a mixing of states cannot occur, since here the $1^B_1$ and $1^A_2$ states go over into $1^A'$ and $1^A''$, respectively. When we translate this result in terms of perturbation theory it would mean that higher order contributions are present and highly anisotropic. This is certainly reflected in the values of the components of the polarizability tensor for the $1^B_1$ state (Table I).

Supermolecule calculations for the neon water dimers (see Table VIII and Fig. 8) support this point of view. Since the neon atom has a spherically symmetric charge distribution no induction contributions are to be expected on the excited water molecule unless by penetration effects. It is seen from Figs. 6 and 8 that indeed in both orientations the first order perturbation theory result and the supermolecule
VIII. GENERAL DISCUSSION AND CONCLUSION

A comparison of our first order and SCF/EHP results for the water dimer with the frozen orbital and generalized valence bond (GVB) results obtained by Guberman and Goddard for different excited Rydberg states of He₂⁴⁶ is enlightening. Apart from the description of the monomers the frozen orbital approach of Ref. 46 is practically equivalent to our complete first order treatment.

In He₂ the long range behavior is completely determined by the exchange repulsion caused by the large Rydberg orbital. For the water dimer this effect is present also, but modified by the electrostatic effects. At shorter distances the excited helium dimer states appear to be repulsive or attractive depending on the nature of the so-called core interaction, since it is assumed that the electron of the diffuse Rydberg orbital moves effectively in the field of a positive dimer ion. In this case the core is the system that remains after removal of this Rydberg electron. In the case of the water dimer the core interaction is attractive for the A'B core, but repulsive for the AB⁺ core, in accordance with the preferred orientation of water molecules around the hydrogen bond between ground state water and positive ions.⁴⁷,⁴⁸ The main difference with the He₂⁺ is that in water both the AB⁺⁺ and A⁺B states are finally repulsive according to the total first order description, indicating that the exchange repulsion always dominates. This may be related to the fact that the considered state of the (H₂O)⁺⁺ complex is not so much a real (delocalized) dimer Rydberg state as the He₂⁺⁺ state.

If the He atomic orbitals are allowed to relax when the two atoms approach, as is the case in the GVB treatment of Ref. 46, it is seen that additional potential wells may appear. These are the result of an avoided crossing, due to mixing of states with higher energy but the same symmetry as the state considered. In the EHP description of the water dimer in the A⁺B state the same situation seems to arise. Whether this attraction has in our case a real physical basis or is, at least partially, an artifact of the excited supermolecule EHP calculation remains to be seen.

Morokuma et al.⁴⁹,⁵⁰ have analyzed the contributions to the hydrogen bond between ground state water and some organic molecules in different electronic states. Using the EHP method (without basis set superposition error corrections) they found that second order contributions were nearly state independent, while first order contributions varied largely. Since the dipole moments of the molecules considered in Refs. 49 and 50 differ considerably in ground and excited states, one would expect at least a varying second order induction contribution, in contrast to what is actually found. This creates the impression that the second order contributions, found from the dimer EHP calculations in Refs. 49 and 50 may be contaminated on a rather large scale with basis set deficiency contributions.

Finally, we can conclude that our calculations, particularly the first order perturbation treatment, give a good insight in the observed spectral blue shift of "solvated" water. It is mainly the large exchange repulsion between a water molecule in the excited state and its neighbors which is responsible. This is both the case for pure water (liquid and ice) and for water in neon matrices. The effects are somewhat dependent on the orientations of the molecules, which can be explained by the shape of the Rydberg state.

Only at very large distances the reversed dipole moment in the excited state causes repulsion between water molecules which are attractive in the ground state. The so-called transition dipole resonance mechanism seems to play a minor role in our case. In geometry I it is completely absent because of symmetry. In the rotated geometries (II) there is a slight decrease in repulsion at those orientations where the transition moments of the two water molecules line up best.

Supermolecule calculations generally give results that compare well with the first order results. Attractive second order (induction) contributions, that can be derived, are larger than in the ground state. Neverthe-

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**TABLE VIII. Binding energies in the water–neon and neon–water dimers obtained from supermolecule calculations.**

<table>
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<tr>
<th>R(Å)</th>
<th>E_{SCF} (A Ne)</th>
<th>E_{EHP} (A⁺⁺ Ne)</th>
<th>E_{SCF} (NeB)</th>
<th>E_{EHP} (NeB⁺⁺)</th>
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</tbody>
</table>
less a blue shift, albeit sometimes small, remains in all cases.

**APPENDIX A: MATRIX ELEMENTS OF THE INTERACTION OPERATOR**

Since the interaction operator is spin free, the most elegant evaluation of the matrix elements would be by the use of a spin free formalism. A derivation of formulas for matrix elements in the case of configurations based on nonorthogonal orbitals, using the fractional parentage decomposition of coordinate wave functions has, to our knowledge, been given only for operators that are symmetric in the electron coordinates.\(^{27}\) The interaction operator, however, is not invariant under permutation of coordinates of electrons belonging to different subsystems. We have therefore chosen for a formulation in terms of Slater determinants. This formulation in terms of Slater determinants is symmetric in operators and wave functions. In the simplest case of closed shell and two open shell singlet states the inconvenience of the use of many determinants for each spin and symmetry eigenfunction, does not yet count. For the ground state we have:

\[
\Psi_A = c_A \alpha^A \prod_{i \in A} \phi_i(x_i)
\]

(A1)

\[
\Psi_B = c_B \alpha^B \prod_{j \in B} \phi_j(x_j).
\]

(A2)

\[c_A = (N_A^+)^{1/2}\]

is the normalizing constant, \(\alpha^A\) the idempotent antisymmetrizer for the \(N_A\) electrons belonging to molecule \(A\), and \(\phi_i\) are the occupied spin-orbitals of molecule \(A\). We will number the spin-orbitals, 1, \(\overline{1}\), 2, \(\overline{2}\), ..., etc. The integers correspond to the molecular orbital number and the absence or presence of the bar indicates a \(\alpha\) or \(\beta\) spin, respectively. The singlet excited state functions are written as:

\[
\Psi_A^*(s-t) = \Psi_A(s-t) - \Psi_A(s-\overline{t})
\]

(A3)

and

\[
\Psi_B^*(u-v) = \Psi_B(u-v) - \Psi_B(\overline{u}-\overline{v}).
\]

(A4)

The notation \(s-t\) indicates that in the product function (A1) the spin-orbital \(s\) (with \(\alpha\) spin) has been replaced by \(t\) (with \(\alpha\) spin as well). The matrix elements to be treated then have the following form:

(a) diagonal

\[
V_{1,1} = \langle \Psi_A^* \Psi_B V \Psi_A^* \Psi_B \rangle = \langle \Psi_A(s-t) \Psi_B V \Psi_A(s-\overline{t}) \Psi_B \rangle - \langle \Psi_A(s-\overline{t}) \Psi_B V \Psi_A(s-t) \Psi_B \rangle
\]

(A5)

(b) off-diagonal

\[
V_{1,11} = \langle \Psi_A^* \Psi_B V \Psi_A \Psi_B^* \rangle = \langle \Psi_A(s-t) \Psi_B V \Psi_A \Psi_B(u-v) \rangle - \langle \Psi_A(s-t) \Psi_B V \Psi_A \Psi_B(\overline{u}-\overline{v}) \rangle.\]

(A6)

Here we have taken into account that the \(s-t\), \(s-\overline{t}\) element gives the same contribution as the \(\overline{s}-\overline{t}\), \(\overline{s}-\overline{t}\) element, etc. When we insert expression (2) for \(V\) in (A5) and (A6), omitting the contribution from \(W_{AB}\) for the moment, we obtain,

\[V_{1,1} = \int \{ \gamma_A^*(s-t, s-t \mid x_1) - \gamma_A^*(s-t, \overline{s}-\overline{t} \mid x_1) \} V_{1A}(1) dx_1 + \int \{ \gamma_B^*(s-t, s-t \mid x_{NA^*}) - \gamma_B^*(s-t, \overline{s}-\overline{t} \mid x_{NA^*}) \} dx_1 dx_{NA^*} + \int \{ \gamma_A^*(s-t, s-\overline{t} \mid x_{NA^*}) - \gamma_A^*(s-t, \overline{s}-\overline{t} \mid x_{NA^*}) \} dx_1 dx_{NA^*} + \int \{ \gamma_B^*(s-t, s-\overline{t} \mid x_{NA^*}) - \gamma_B^*(s-t, \overline{s}-\overline{t} \mid x_{NA^*}) \} dx_1 dx_{NA^*}
\]

(A7)

\[V_{1,11} = \int \{ \gamma_A^*(s-t, u-v \mid x_1) - \gamma_A^*(s-t, \overline{u}-\overline{v} \mid x_1) \} V_{1A}(1) dx_1 + \int \{ \gamma_B^*(s-t, u-v \mid x_{NA^*}) - \gamma_B^*(s-t, \overline{u}-\overline{v} \mid x_{NA^*}) \} dx_1 dx_{NA^*} + \int \{ \gamma_A^*(s-t, \overline{u}-\overline{v} \mid x_{NA^*}) - \gamma_A^*(s-t, u-v \mid x_{NA^*}) \} dx_1 dx_{NA^*} + \int \{ \gamma_B^*(s-t, \overline{u}-\overline{v} \mid x_{NA^*}) - \gamma_B^*(s-t, u-v \mid x_{NA^*}) \} dx_1 dx_{NA^*}
\]

(A8)

Here \(x_1\) is an electron coordinate on \(A\) and \(x_{NA^*}\) on \(B\). The TIDM's used in (A7) and (A8) are defined by

\[
\begin{align*}
\gamma_A^*(s-t, s-t) &= c_A \alpha^A \prod_{i \in A} \phi_i(x_i) \\
\gamma_A^*(s-t, \overline{s}-\overline{t}) &= c_A \alpha^A \prod_{i \in A} \phi_i(x_i) \\
\gamma_B^*(s-t, s-\overline{t}) &= c_B \alpha^B \prod_{j \in B} \phi_j(x_j) \\
\gamma_B^*(s-t, \overline{s}-\overline{t}) &= c_B \alpha^B \prod_{j \in B} \phi_j(x_j)
\end{align*}
\]
\[ \gamma_1^A(s-t,s-t|x_1) = N \sum \int \Psi_A(s-t|x_1 \cdots x_n) \Psi_B(x_{N+1} \cdots x_n) \alpha_A(s-t|x_1 \cdots x_n) \Psi_B(x_{N+1} \cdots x_n) dx_2 \cdots dx_n \]  

(A9)

\[ \gamma_1^A(s-t,u-v|x_1) = N \sum \int \Psi_A(s-t|x_1 \cdots x_n) \Psi_B(x_{N+1} \cdots x_n) \alpha_A(x_1 \cdots x_n) \Psi_B(u-v|x_{N+1} \cdots x_n) dx_2 \cdots dx_n \]  

(A10)

We have, of course, analogous expressions for \( \gamma_1^B \) etc.

\[ \gamma_1^{AB}(s-t,s-t|x_{N+1}) = N_A N_B \sum \int \Psi_A(s-t|x_1 \cdots x_n) \Psi_B(x_{N+1} \cdots x_n) \times \alpha_A(s-t|x_1 \cdots x_n) \Psi_B(x_{N+1} \cdots x_n) \times \cdots dx_2 \cdots dx_n dx_{N+2} \cdots dx_N \]  

(A11)

\[ \gamma_2^{AB}(s-t,u-v|x_{N+1}) = N_A N_B \sum \int \Psi_A(s-t|x_1 \cdots x_n) \Psi_B(x_{N+1} \cdots x_n) \times \alpha_A(x_1 \cdots x_n) \Psi_B(u-v|x_{N+1} \cdots x_n) \times \cdots dx_2 \cdots dx_n dx_{N+2} \cdots dx_N \]  

(A12)

\[ (N = N_A + N_B) \]

The TIDM's given in (A9) and (A11) appear in the diagonal element, just as the analogues with \((s-t, s-t)\). In the off-diagonal elements also the type with \((s-t, u-v)\) in (A10) and (A12) arises. Since we have so far considered explicitly spin orbital products, we can directly use the result given in equation (A9) from Ref. 27 for the first order TIDM's and Eq. 23 for the second order TIDM's. In our notation we obtain for instance for the first order TIDM

\[ \gamma_1^A(s-t,s-t|x_1) = c \sum_i \sum_p (-1)^{i+p} \phi_i(x_1) \phi_p(x_1) D_{1p}(s-t,s-t) \]  

(A13)

with

\[ c = \frac{N_A! N_B!}{N!} \]

In (A13) the summation index \( i \) runs over the spin orbitals contained in \( \Psi_A(s-t) \) and \( p \) runs over the spin orbitals in the combined set of \( \Psi_A(s-t) \) and \( \Psi_B \). \( D_{1p}(s-t,s-t) \) is the first order minor obtained by removal of the \( i \)th row and the \( p \)th column from the overlap matrix \( S(s-t,s-t) \) with row and column indices determined by the spin orbitals present in \( \Psi_A(s-t) \) and \( \Psi_B \). The minor can be found from the inverse of the overlap matrix by application of Jacobi's ratio theorem.\(^{32}\)

\[ (-1)^{i+p} D_{1p}(s-t,s-t) = D(s-t,s-t) S_{11}^{-1}(s-t,s-t) \]

(D is the determinant of the matrix \( S \). A condition of course is that \( S \) is nonsingular. (If \( S \) becomes singular, for instance by symmetry, one has to continue the derivation in terms of minors. In actual computations, however, such a singularity may be lifted by introducing some small perturbation causing only negligible errors in the final results, provided the computer programs are stable enough.)

The final result for the diagonal first order TIDM is therefore

\[ \gamma_1^A(s-t,s-t|x_1) = c D(s-t,s-t) \sum_i \sum_p (-1)^{i+p} \phi_i(x_1) \phi_p(x_1) S_{11}^{-1}(s-t,s-t) \]  

(A15)

For the off-diagonal first order TIDM we have

\[ \gamma_1^A(s-t,u-v|x_1) = c \sum_i \sum_p (-1)^{i+p} \phi_i(x_1) \phi_p(x_1) D_{1p}(s-t,u-v) \]  

(A16)

The index \( p \) runs over a different set of spin orbitals compared with (A13). The minor \( D_{1p}(s-t,u-v) \) is now obtained from the nonsymmetric overlap matrix \( S(s-t,u-v) \) with the row indices given by the spin orbitals in \( \Psi_A(s-t) \) and the column indices by those in \( \Psi_B(u-v) \). In analogy with (A15) we obtain

\[ \gamma_1^A(s-t,u-v|x_1) = c D(s-t,u-v) \sum_i \sum_p (-1)^{i+p} \phi_i(x_1) \phi_p(x_1) S_{11}^{-1}(s-t,u-v) \]  

(A17)

Expressions for second order TIDM's can be found using the same reasoning. For an off-diagonal TIDM we find, for instance

\[ \gamma_2^{AB}(s-t,u-v|x_{N+1}) = c D(s-t,u-v) \sum_i \sum_p \sum_{s,t} \sum_{j,k} \phi_i(x_1) \phi_p(x_1) \phi_s(x_{N+1}) \phi_t(x_{N+1}) d(S_{11}^{-1}(s-t,u-v) S_{11}^{-1}(s-t,u-v)) \]  

(A18)

The final one and two electron contributions to the (off-diagonal) element of the interaction operator thus have the form
\[ V_{1A}(s-t, u-v) = cD(s-t, u-v) \sum_{i}^{A(s-t)} \sum_{p}^{B(u-v)} S_{pi}^{-1}(s-t, u-v) v_{1AIP} \]

with
\[ v_{1AIP} = \int \phi_i(x_1) V_{1A}(1) \phi_p(x_1) dx_1 \]  
(A19)

and
\[ G_{2AB}(s-t, u-v) = cD(s-t, u-v) \sum_{i}^{A(s-t)} \sum_{p}^{B(u-v)} \sum_{q}^{B(u-v)} d[S_{pi}^{-1}(s-t, u-v) S_{qk}^{-1}(s-t, u-v)] (ip | kq) \]  
(A20)

with
\[ (ip | kq) = \int \phi_i(x_1) \phi_p(x_1) \frac{1}{f_{1, A_{k-1}}} \phi_q(x_{N_{A_k}}) \phi_q(x_{N_{A_k}}) dx_1 dx_{N_{A_k}} \]  
(A21)

In all these expressions the summations run over spin orbitals. The separation of contributions of \( \alpha \) and \( \beta \) spins is somewhat more cumbersome than for the closed shell case treated in Ref. 27, due to the occurrence of open shells. To proceed we order the list of spin orbitals in such a way that all \( \alpha \) spin orbitals appear first. The \( S \) matrix in (A17), for instance, has the form as given in Fig. A1 for the case of water (5 occupied molecular orbitals in the ground state, the singly excited state obtained by excitation from molecular orbital 5 to 6 on molecule A and similarly for \( \Psi_0^{A} \)). The determinant \( D(s-t, u-v) \) is thus seen to be the product of the determinants of the two not necessarily symmetric overlap matrices for \( \alpha \) and \( \beta \) spin. So we can write \( D(s-t, u-v) = D' D''(s-t, u-v) \), where \( D' \) is a determinant of an overlap matrix based on molecular orbitals. Also the inverse of \( S \) is the combination of \( \alpha \) and \( \beta \) spin orbital overlap matrices. The summations in (A19) and (A20) thus can be performed separately over the \( \alpha \) and \( \beta \) spin orbitals. From here on we will consider only molecular orbital numbers as labels (running indices) in the summation. When we perform the separate summation we obtain for (A19)

\[ V_{1A}(s-t, u-v) = cD' D''(s-t, u-v) v \left[ \sum_{i}^{A(s-t)} \sum_{p}^{A(u-v)} v_{1AIP} S_{pi}^{-1} \right] \]  
(A22)

and for (A20)

\[ G_{2AB}(s-t, u-v) = cD' D''(s-t, u-v) v \left[ \sum_{i}^{A(s-t)} \sum_{p}^{A(u-v)} \sum_{q}^{A(u-v)} (ip | kq) d[S_{pi}^{-1} S_{pq}^{-1}] + \sum_{i}^{A(s-t)} \sum_{p}^{A(u-v)} \sum_{q}^{A(u-v)} (ip | kq) d[S_{pi}^{-1} S_{pq}^{-1}] \right] \]  
(A23)

Here we adhered to the convention that \( i \) runs over the ground state molecular orbitals of \( A \) unless replacement of occupied orbitals \( s \) by an excited state orbital \( t \) is indicated above the summation sign. Similarly \( k \) is on \( B \), etc. \( p \) and \( q \) run over the combined set of ground state molecular orbitals of \( A \) and \( B \) unless replacement is indicated. Expressions for the remaining terms in (A8) can be found along the same lines, just as the formulas for the three other matrix elements of the interaction operator. The full expressions take up much space but are nevertheless easy to program. All one has to know are the summation ranges; they determine the composition of overlap matrices and determinants completely.

We conclude with the remark that the \( S_{11,1} \), \( S_{11,11} \), \( S_{11,1} \), and \( S_{11,11} \) matrix elements can be found using the standard rules for the evaluation of matrix elements for configurations based on nonorthogonal orbitals.\(^{19}\) Also from the derivation given before it is immediately seen that

\[ S_{11,1} = c[D' D''(s-t, s-t) - D'(s-t, -) D''(s-t, -)] \]  
(A24)

\[ S_{11,11} = c[D' D''(s-t, u-v) - D'(s-t, -) D''(-, u-v)] \]  
(A25)

\[ S_{11,11} = c[D' D''(u-v, u-v) - D'(-, u-v) D''(-, u-v)] \]  
(A26)


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