Calculation of exchange forces between molecules by application of the Hellmann–Feynman theorem

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(Received 28 September 1976; revision received 11 January 1977)

The computation of exchange forces between molecules can be performed about 20 times faster by using the Hellmann–Feynman theorem than by the usual energy methods. The accuracy of the results for He₂, He–H₂, (H₂O)₂ and (C₂H₄)₂ is disappointing, however, particularly in the region of the Van der Waals minimum.

1. Introduction

Although most applications of the Hellmann–Feynman theorem are concerned with molecular structure [1], occasionally this theorem has also been used for the calculation of intermolecular forces. Following a suggestion in the original paper by Feynman [2], long-range Van der Waals forces have been evaluated by invoking the Hellmann–Feynman theorem for two ground-state hydrogen atoms by Hirschfelder and Eliason [3] and, more recently, for H . . . H⁺ and for H(1s) . . . H(2p) by Nakatsuji and Koga [4]. Bader [5] and Salem [6] have shown that the theorem provides a direct route to the calculation of the (Pauli) exchange repulsion between non-bonding (helium) atoms. Most authors seem to agree, however, that the use of the Hellmann–Feynman theorem is rather unattractive for actual calculations, since the forces calculated are generally more sensitive to errors in the wave function than the energy expectation values. Salem and Wilson [7] have pointed out in a very illustrative paper that the use of approximate wave functions may lead to Hellmann–Feynman forces which are even qualitatively incorrect. Moreover, they showed that the (perturbational) calculation of the forces requires the use of wave functions of higher order than needed for the calculation of the perturbation energies to the same accuracy.

Not much experience is available, however, in the evaluation of intermolecular exchange forces with the Hellmann–Feynman theorem at intermediate distances, i.e. in the region of the Van der Waals minimum. The molecular studies normally look at chemical bonding distances, and even calculations of exchange forces between non-bonding atoms [5, 6] have considered rather short-range effects. Moreover, the latter calculations have, to our knowledge, never been extended to obtain the forces between molecules. Such calculations may be of great interest for the following reason. The \textit{ab initio} computation of Van der Waals forces including the repulsive short-range part and the (mainly) attractive long-range interactions, although possible in one consistent formalism [8], requires the evaluation of so many electronic interaction integrals that such a
treatment of systems much larger than, for example, the ethylene dimer con-
sidered in reference [8] will be prohibitively expensive, at least in the near future. 
After separating the short-range exchange repulsions and the long-range forces 
in the usual manner, the latter can be calculated much more simply by invoking 
the multipole expansion of the intermolecular interaction operator, because, in 
that case, only intramolecular integrals have to be computed. For the remaining 
exchange forces one then needs a method of calculation which equally avoids 
or simplifies the computation of intermolecular integrals, especially the time-
consuming two-electron ones. As will be illustrated in this paper, the Hellmann– 
Feynman theorem may provide such a computationally simple method; its 
accuracy has been tested on several molecular dimers: He₂, He–H₂, (H₂O)₂, 
(C₂H₄)₂.

2. Theory

The (electrostatic) Hellmann–Feynman theorem states that, in atomic or 
molecular systems, the forces \( \mathbf{F}_a \) on a nucleus \( \alpha \) can be calculated by classical 
electrostatics from the positions \( \mathbf{R}_\beta \) of the other nuclei treated as point charges 
\( Z_\beta \) and from the electronic charge density distribution, \( \rho(r) \), calculated quantum 
mechanically, so

\[
\mathbf{F}_\alpha = - \langle \nabla_a H \rangle = Z_\alpha \left[ \sum_{\beta \neq \alpha} \frac{Z_\beta(\mathbf{R}_\alpha - \mathbf{R}_\beta)}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|^3} - \int \frac{\rho(r)(\mathbf{R}_\alpha - r)}{|\mathbf{R}_\alpha - r|^3} \, dr \right].
\]

(1)

The theorem has been derived for exact wave functions; for approximate wave 
functions the force calculated according to the Hellman–Feynman formula (1) 
will generally differ from the force obtained by differentiating the energy 
expectation value. Although either force can be considered as an approximation 
to the exact force, in many cases the latter approximation will be the better one. 
Only for special approximate wave functions [9], for instance exact Hartree–Fock 
functions [10] or wave functions expanded in a ‘ floating ’ basis which is variation-
onally optimized [11], will the two approximate forces be equal.

With regard to the problem we are interested in, i.e. the interactions between 
two closed-shell molecules A and B, we assume the ground-state wave functions 
\( \phi_A(0) \) and \( \phi_B(0) \) to be known. In practice these will be approximate Hartree– 
Fock functions written as Slater determinants composed of LCAO–MO’s on A 
and B. An approximate wave function for the dimer is given by the anti-
symmetrized product \( \mathcal{A} \phi_A(0) \phi_B(0) \), where \( \mathcal{A} \) is the antisymmetrizer with respect 
to intermolecular permutations. Although this wave function is still of zeroth 
order in the interaction operator \( V_{AB} \), the mere antisymmetrization already 
causes the electronic charge density to decrease in the overlap region between the 
molecules A and B and to pile up in the outer regions of the dimer. As Salem 
[6] has pointed out, the substitution of this charge density into the Hellmann– 
Feynman formula (1) yields a repulsive force on the nuclei which corresponds to 
the Pauli or exchange repulsion.

This procedure can easily be extended to molecular systems by vectorially 
adding the forces on all nuclei of a given molecule in order to obtain the force 
on that molecule. Still, this extension causes two problems. The first one is 
rather trivial: the forces on the nuclei calculated from the monomer functions 
may be non-zero already, because, either these (approximate) wave functions do
not satisfy the Hellmann–Feynman theorem or the nuclei have not been relaxed to their theoretical equilibrium positions. Assuming additivity, one can easily correct for this effect by subtracting from the total force on a given nucleus $\alpha$ the contributions which arise from the monomer charge distribution of $A$.

The second problem is due to the fact that the wave function $\mathcal{A}\phi_\alpha^{(0)}\phi_B^{(0)}$ is only an approximate dimer function, for which the Hellmann–Feynman theorem certainly does not hold. Particularly in the case of molecules, which possess permanent multipole moments, this leads to artifacts of the type described by Salem and Wilson for an atom in an electric field [7]. This is readily seen in the asymptotic limit of $R \rightarrow \infty$ where the effect of the antisymmetrization vanishes and the charge distribution calculated from $\mathcal{A}\phi_\alpha^{(0)}\phi_B^{(0)}$ becomes equal to $\rho_\alpha^{(0)} + \rho_B^{(0)}$. Making a perturbation expansion in terms of the interaction operator $V_{AB}$, the first-order contribution to the Hellmann–Feynman force reads

$$-F^{(1)}_\alpha = \langle \psi^{(0)} | \nabla_x V_{AB} | \psi^{(0)} \rangle + \langle \psi^{(0)} | \nabla_x H^{(0)} | \psi^{(1)} \rangle + \langle \psi^{(1)} | \nabla_x H^{(0)} | \psi^{(0)} \rangle$$

with $H^{(0)} = H_A + H_B$ and $\psi^{(0)} = \phi_\alpha^{(0)}\phi_B^{(0)}$. This expression, by contrast with the first-order energy formula, contains terms which are first order in the wave function and, thus, cannot be obtained from the unperturbed charge distribution $\rho_\alpha^{(0)} + \rho_B^{(0)}$ alone. This unperturbed charge distribution yields only the first term in expression (2), which represents the effect of the electric field originating from $\rho_B^{(0)}$ and acting on the bare nuclei of $A$ [7].

In the total first-order expression (2) this force on the bare nuclei will be compensated by the screening effect of the electrons on $A$, which is described by the last two terms in (2). This screening is accounted for by the polarized, first-order corrected, charge density $\rho^{(1)} = \psi^{(0)}\psi^{(1)} + \psi^{(1)}\psi^{(0)}$ on $A$ exerting a force on the nuclei $\alpha$ of $A$. A complete cancellation of the terms in (2) will occur if the subsystems are non-polar; otherwise the residual force is precisely the electrostatic force between the monomers. So, the Hellmann–Feynman theorem only includes the electronic screening, which of course we know to be present physically, if the forces are calculated from first-order charge distributions.

By extending the calculations up to $F^{(2)}_\alpha$, which requires the knowledge of second-order wave functions†, one will find the induction and dispersion contributions to the Van der Waals interaction energy [3, 4].

The polarization corrections to the unperturbed charge density $\rho_\alpha^{(0)} + \rho_B^{(0)}$, which are needed to calculate the correct first-order Hellmann–Feynman force on a molecule (and not just the force on the bare nuclei), can also be obtained from a variational method. Calculating a wave function which satisfies the Hellmann–Feynman theorem for the dimer $AB$, for instance an exact Hartree–Fock function (or a Hartree–Fock LCAO function at the Hartree–Fock limit) or a fully optimized ‘floating orbital’ wave function, one automatically includes the proper screening contributions to the Hellmann–Feynman force.

Both the variational and the perturbational calculation of the polarization corrections to the wave function $\mathcal{A}\phi_\alpha^{(0)}\phi_B^{(0)}$, require the calculation of matrix

† Recently, Koga and Nakatsuji [12] have proposed a formalism, based on the Hellmann–Feynman theorem, for the calculation of the total force between whole subsystems. They differentiate the hamiltonian with respect to $R_{AB}$, a parameter which only occurs in $V_{AB}$, not in $H^{(0)}$. Although this avoids the necessity of calculating wave functions up to $n$th order for obtaining the $n$th-order force, the effort to compute $F^{(n)}$ by this method is at least the same as for a direct calculation of the $n$th-order perturbation energy.
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elements over $V_{AB}$, however, which amounts to at least the same computational effort as calculating the energy expectation value for the dimer. Therefore, we have chosen to study a much simpler solution, which only needs the un­

perturbed wave function. In the present paper we are not interested in the long-range electrostatic, induction or dispersion forces, but only in the exchange interactions. We have calculated the exchange forces on the nuclei according to the following definition:

$$-F_{\alpha}^{\text{ex}} = \langle \nabla_{\alpha} H \rangle_{\phi_A^{(\mu)} \phi_B^{(\nu)}} - \langle \nabla_{\alpha} H \rangle_{\phi_A^{(\nu)} \phi_B^{(\mu)}}$$

(3)

which amounts to using formula (1) with an electronic charge distribution $\rho(r)$ obtained from the wave function $\phi_A^{(0)} \phi_B^{(0)}$ and subtracting the forces due to the unperturbed distribution, $\rho_A^{(0)} + \rho_B^{(0)}$. This avoids both problems discussed above and yields directly the pure exchange forces which originate from the difference in electronic density due to the antisymmetrization. The drawback of this 'difference density' approach is that the (short range) effects on the electrostatic interactions between the monomers, resulting from the penetration of their charge distributions, are also subtracted out, but these effects are smaller than the pure exchange effects particularly in the neighbourhood of the Van der Waals minimum [13] (see also tables 1 and 2).

The whole procedure is computationally very simple, indeed, because the effect of the antisymmetrization on the electron density can be obtained, for closed-shell systems, by orthogonalization of the monomer MO’s on A and B. The calculation can be carried out with a standard molecular programme package such as IBMOL-5A [14], including a subroutine for electric-field-strength calculations and supplemented with an orthogonalization routine. It is very fast, since the only dimer integrals that have to be evaluated are the nuclear attraction integrals that are required for the computation of formula (1).

3. Results

Salem [6] has computed the exchange force between two helium atoms in the repulsive region using single-zeta or double-zeta Slater-type orbitals (STO’s) for the atomic 1s functions. We have repeated his calculations including somewhat larger $R$ values, lying around the Van der Waals minimum, using six gaussian-type orbitals (GTO’s) for the 1s functions (which yields about the same quality as two STO’s) and also with ten GTO’s. In table 1 these results are listed, together with the forces obtained by differentiating energy expectation values calculated with the same wave functions. Since one is usually interested in potential energy curves rather than forces, we have also calculated those by integrating the forces and compared them in table 2 with exchange interaction potentials from energy expectation values‡.

‡ Both the differentiation of $\Delta E(R)$ and the integration of the $F(R)$ curves were performed analytically after making a (logarithmic) least-squares fit to the calculated points, using functions of the type: $\exp (-a - bR - cR^2)$. In the case of He–H$_2$, (H$_2$O)$_2$ and (C$_2$H$_4$)$_2$ we added a cubic term to the exponent. Several other methods of differentiation and integration have been tried; for instance, a cubic spline fit through the logarithms of the energy values or a linear interpolation of these logarithms; the results obtained are all in rather close agreement.
Table 1. Exchange forces in He . . . He for different A.O. bases (a).

<table>
<thead>
<tr>
<th>$R(f)$ (bohr)</th>
<th>1 STO (d)</th>
<th>2 STO’s (d)</th>
<th>6 GTO’s (e)</th>
<th>10 GTO’s (e)</th>
<th>Gradient of $\Delta E^{ex}$ (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>(7019)</td>
<td>(9104)</td>
<td>7983</td>
<td>(9115)</td>
<td>8009 (9144)</td>
</tr>
<tr>
<td>3.0</td>
<td>(1900)</td>
<td>(2892)</td>
<td>2627</td>
<td>(2884)</td>
<td>2651 (2907)</td>
</tr>
<tr>
<td>3.5</td>
<td>(492)</td>
<td>(896)</td>
<td>855</td>
<td>(912)</td>
<td>850 (909)</td>
</tr>
<tr>
<td>4.0</td>
<td>(123)</td>
<td>(271)</td>
<td>271</td>
<td>(282)</td>
<td>266 (280)</td>
</tr>
<tr>
<td>4.5</td>
<td>(30)</td>
<td>(80)</td>
<td>80</td>
<td>(82)</td>
<td>81 (84)</td>
</tr>
<tr>
<td>5.0</td>
<td>(7.0)</td>
<td>(23)</td>
<td>22</td>
<td>(22)</td>
<td>24 (25)</td>
</tr>
<tr>
<td>5.5</td>
<td>5.4</td>
<td>(5.4)</td>
<td>7.2</td>
<td>(7.4)</td>
<td>10.1 (8.7)</td>
</tr>
<tr>
<td>6.0</td>
<td>1.2</td>
<td>(1.2)</td>
<td>2.2</td>
<td>(2.2)</td>
<td>2.8 (2.4)</td>
</tr>
<tr>
<td>6.5</td>
<td>0.2</td>
<td>(0.2)</td>
<td>0.6</td>
<td>(0.6)</td>
<td>0.7 (0.7)</td>
</tr>
</tbody>
</table>

(a) Results in $10^{-5}$ hartree/bohr; 1 hartree/bohr $= 8.2378 \times 10^{-8}$ J/m.
(b) Defined in formula (3); (in parentheses: the value of the first term).
(c) Defined in formula (4); (in parentheses: the gradient of the first term, $\Delta E^{tot}$).
(d) Results from Salem, reference [6].
(e) Exponents and contraction coefficients from reference [15].
(f) 1 bohr $= 5.29167 \times 10^{-11}$ m.
Table 2. Exchange interactions in He...He for different A.O. bases (a).

<table>
<thead>
<tr>
<th>$R$ (bohr)</th>
<th>Integrated force (b)</th>
<th>$\Delta E^{ex}$ (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 GTO's (d)</td>
<td>10 GTO's (d)</td>
</tr>
<tr>
<td>2.5</td>
<td>3572 (3950)</td>
<td>3581 (3966)</td>
</tr>
<tr>
<td>3.0</td>
<td>1219 (1309)</td>
<td>1148 (1243)</td>
</tr>
<tr>
<td>3.5</td>
<td>383 (402)</td>
<td>361 (383)</td>
</tr>
<tr>
<td>4.0</td>
<td>111 (114)</td>
<td>112 (116)</td>
</tr>
<tr>
<td>4.5</td>
<td>29 (30)</td>
<td>34 (35)</td>
</tr>
<tr>
<td>5.0</td>
<td>7.3 (7.3)</td>
<td>10.1 (10.3)</td>
</tr>
<tr>
<td>5.5</td>
<td>1.6 (1.6)</td>
<td>2.9 (3.0)</td>
</tr>
<tr>
<td>6.0</td>
<td>0.34 (0.34)</td>
<td>0.85 (0.85)</td>
</tr>
<tr>
<td>6.5</td>
<td>0.07 (0.07)</td>
<td>0.24 (0.24)</td>
</tr>
</tbody>
</table>

(a) Results in $10^{-5}$ hartree; 1 hartree $= 4.3592 \times 10^{-18}$ J.

(b) Defined as: $\int_{\infty}^{R} F^{ex}(R) dR$ with $F^{ex}$ from formula (3); (in parentheses: the first term).

(c) Defined in formula (4); (in parentheses: the first term, $\Delta E^{tot}$).

(d) Exponents and contraction coefficients from reference [15].
The deviations of the Hellmann–Feynman results from the energy results are rather large: typically a factor of 1.5. The Hellmann–Feynman forces are more sensitive also to the quality of the long-range tail of the wave function, which is obviously lower for six GTO's. The electrostatic interaction terms, which only arise from penetration in this case, because both subsystems are non-polar, are indeed smaller than the pure exchange effects. (In the region of the Van der Waals minimum they are about 15 per cent of these.) If we omit the correction of the exchange forces with these terms, the agreement between the Hellmann–Feynman force and the energy is somewhat better, but we cannot do this when we are dealing with molecular subsystems because of the problems discussed in the previous section.

One of the simplest systems involving a molecule is the He...H₂ dimer for which we have already calculated potential energy curves including Van der Waals interactions [16]. The H₂ energy for the 6s, 2p, 1d GTO basis used was very near to the Hartree–Fock limit and it was verified that the H₂ wave functions closely satisfied the Hellmann–Feynman theorem. The H–H distance taken (1.40 bohr) was not optimized but is rather close to the equilibrium value for this wave function. Small forces on the H nuclei resulting from the monomer H₂ charge distribution obviously cannot yield a net force on the molecule because of symmetry. In table 3 the Hellmann–Feynman forces on the He atom and on the H₂ molecule are compared with the exchange forces derived from energy expectation values. Since the H₂ molecule in the ground state has a quadrupole moment it is essential that for the calculation of the Hellmann–Feynman exchange force on He the procedure described in the previous section (formula (3)) is followed.

Table 3. Exchange forces in He...H₂(a), (b).

<table>
<thead>
<tr>
<th>R (bohr)</th>
<th>(F_{\text{He}^\text{ex}})</th>
<th>(F_{\text{H}_2^\text{ex}})</th>
<th>Gradient of (\Delta E^\text{ex})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linear geometry (c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3·0</td>
<td>-8353</td>
<td>4879</td>
<td>11278</td>
</tr>
<tr>
<td>4·0</td>
<td>-1375</td>
<td>720</td>
<td>1604</td>
</tr>
<tr>
<td>5·0</td>
<td>-199</td>
<td>90</td>
<td>216</td>
</tr>
<tr>
<td>5·5</td>
<td>-72</td>
<td>30</td>
<td>77</td>
</tr>
<tr>
<td>6·0</td>
<td>-25</td>
<td>8·9</td>
<td>27</td>
</tr>
<tr>
<td>6·5</td>
<td>-8·4</td>
<td>2·5</td>
<td>9·1</td>
</tr>
<tr>
<td>8·0</td>
<td>-0·2</td>
<td>0·0</td>
<td>0·3</td>
</tr>
<tr>
<td>Perpendicular geometry (c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3·0</td>
<td>-5590</td>
<td>3463</td>
<td>7467</td>
</tr>
<tr>
<td>4·0</td>
<td>-928</td>
<td>508</td>
<td>1089</td>
</tr>
<tr>
<td>5·0</td>
<td>-149</td>
<td>61</td>
<td>148</td>
</tr>
<tr>
<td>5·5</td>
<td>-50</td>
<td>19</td>
<td>53</td>
</tr>
<tr>
<td>6·0</td>
<td>-17</td>
<td>5·4</td>
<td>18</td>
</tr>
<tr>
<td>6·5</td>
<td>-5·4</td>
<td>1·6</td>
<td>6·2</td>
</tr>
<tr>
<td>8·0</td>
<td>-0·2</td>
<td>0·0</td>
<td>0·2</td>
</tr>
</tbody>
</table>

(a) Results in \(10^{-5}\) hartree/bohr.
(b) Basis sets: He(6s), H(6s, 2p, 1d). For contraction coefficients, exponents and lowest H₂-M.O. see reference [16].
(c) See reference [16] for the atomic coordinates.
The results in table 3 show that the Hellmann–Feynman force on the He atom is not equal to the force on H\(_2\), as is not necessary when using approximate wave functions. It is striking, however, that the force on He agrees reasonably well with the energy derivative, whereas the force on H\(_2\) shows much larger deviations, especially for large \(R\).

In order to make more conclusive tests for molecules, we have also studied the H\(_2\)O dimer and the C\(_2\)H\(_4\) dimer for which Van der Waals potentials including exchange energies were available [8, 13, 17]. For the water molecule the same (11, 7, 2/6, 1) GTO basis as in reference [17] was used; the monomer MO’s were kindly provided by one of the authors [18]. For the ethylene dimer we have investigated the two different relative orientations of the molecules considered in reference [8] and used the same (6, 3/3) basis set and the same monomer MO’s. Moreover, we have calculated the Hellmann–Feynman forces in a more extended (9, 5, 1/4, 1) basis set on C\(_2\)H\(_4\), taken from reference [13], although the exchange force from the energy expectation value was not yet available for this basis, due to the heavy computations required for the dimer energy calculation. The exchange forces calculated from the Hellmann–Feynman theorem by using formula (3) are compared in tables 4 and 5 with the forces obtained from one of the two following exchange interaction energy definitions:

\[
\Delta E^{\text{ex}} = \Delta E^{\text{tot}} - \Delta E^{\text{elec}}
\]

with

\[
\Delta E^{\text{tot}} = \langle H \phi_A^{(n)} \phi_B^{(n)} \rangle - \langle H_A \phi_A^{(n)} \rangle - \langle H_B \phi_B^{(n)} \rangle
\]

and

\[
\Delta E^{\text{elec}} = \langle V_{AB} \phi_A^{(n)} \phi_B^{(n)} \rangle
\]

or

\[
\mathcal{P}_{AB}^{\text{ex}} = \mathcal{P}_{AB} - \Delta E^{\text{elec}}
\]

with

\[
\mathcal{P}_{AB} = \langle \phi_A^{(0)} \phi_B^{(0)} | V_{AB} | \phi_A^{(0)} \phi_B^{(0)} \rangle / \langle \phi_A^{(0)} \phi_B^{(0)} | \phi_A^{(0)} \phi_B^{(0)} \rangle.
\]

The latter definition is usually obtained as the first-order interaction energy in perturbation theories including exchange effects.

One observes again, in all cases where the symmetry does not prevent this, that the forces on the two monomers are significantly different. The deviations of the Hellmann–Feynman forces from the energy derivatives are also considerable, especially for large \(R\). It seems very strange that, contrary to the energy results, the Hellmann–Feynman calculations predict in some cases the exchange forces to be attractive for large distances. This effect can be explained by looking at the forces on the individual nuclei in the monomers, which are usually repulsive for those nuclei that are close to the second monomer, but are attractive for some other nuclei in more distant regions of the monomers. Since all the forces are in error, due to the approximate nature of the wave functions, it can easily occur that the net forces have the wrong sign, thus leading to another artifact arising from the use of the Hellmann–Feynman theorem with approximate charge distributions.
Table 4. Exchange forces in H₂O . . . H₂O (a), (b).

<table>
<thead>
<tr>
<th>R (bohr)</th>
<th>$F_{H_2O_A}^{ex}$</th>
<th>$F_{H_2O_B}^{ex}$</th>
<th>Gradient of $\Delta E^{ex}$</th>
<th>Gradient of $\mathcal{F}_{AB}^{ex}$ (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4·0</td>
<td>-14401</td>
<td>23364</td>
<td>23403</td>
<td>28684</td>
</tr>
<tr>
<td>4·4</td>
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<td>15867</td>
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<td>4·8</td>
<td>-2430</td>
<td>3329</td>
<td>9319</td>
<td>7394</td>
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<td>5·2</td>
<td>-1127</td>
<td>1168</td>
<td>4879</td>
<td>3626</td>
</tr>
<tr>
<td>5·67</td>
<td>-430</td>
<td>259</td>
<td>2032</td>
<td>1521</td>
</tr>
<tr>
<td>7·0</td>
<td>-9·7</td>
<td>-33·6</td>
<td>111</td>
<td>106</td>
</tr>
<tr>
<td>9·0</td>
<td>0·9</td>
<td>-0·8</td>
<td>1·2</td>
<td>1·0</td>
</tr>
</tbody>
</table>

(a) Results in $10^{-5}$ hartree/bohr.
(b) Atomic coordinates, A.O. basis and M.O.'s from reference [17], R taken along x-axis.
(c) $\mathcal{F}_{AB}^{ex}$ is defined in formula (5).

Table 5. Exchange forces in C₂H₄ . . . C₂H₄ (a).

<table>
<thead>
<tr>
<th>R (bohr)</th>
<th>$F_{C_2H_4}^{ex}$ (c)</th>
<th>Gradient of $\Delta E^{ex}$ (c)</th>
<th>$F_{C_2H_4}^{ex}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4·0</td>
<td>48063</td>
<td>48914</td>
<td>49027</td>
</tr>
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<td>5·0</td>
<td>10064</td>
<td>8901</td>
<td>14352</td>
</tr>
<tr>
<td>6·0</td>
<td>1498</td>
<td>1684</td>
<td>3606</td>
</tr>
<tr>
<td>7·0</td>
<td>158</td>
<td>291</td>
<td>707</td>
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<tr>
<td>8·0</td>
<td>12·0</td>
<td>40·4</td>
<td>106</td>
</tr>
<tr>
<td>9·0</td>
<td>1·2</td>
<td>3·9</td>
<td>13·2</td>
</tr>
</tbody>
</table>

(a) Results in $10^{-5}$ hartree/bohr.
(b) Atomic coordinates from reference [8].
(c) Split-valence basis from reference [8]: C(6s, 3p), H(3s).
(d) Basis C from reference [13]: C(9s, 5p, 1d), H(4s, 1p).

For the water dimer, where the exchange interaction energy has been calculated in two different ways [18], definition (5) yields a slightly weaker repulsion than the energy expectation value difference (4). This is in agreement with the experience [19] that formula (5) tends to underestimate the exchange energy.
when used with approximate monomer wave functions. The Hellmann–Feynman theorem gives a much stronger underestimate of the exchange forces in this case.

Also for the ethylene dimer the Hellmann–Feynman forces predict much weaker repulsions than the energy expectation values when calculated with the same basis, at least for large $R$. Moreover, we can conclude from table 5 that the Hellmann–Feynman forces are rather sensitive to the quality of the basis set.

4. Conclusions

The Hellmann–Feynman method of calculating intermolecular exchange forces as described in this paper is computationally much faster than the energy methods, typically by a factor of 20, since the time-consuming calculation of all intermolecular two-electron integrals is avoided.

From the results presented in the previous section we must conclude, however, that the Hellmann–Feynman method yields large deviations from the results of energy methods, the latter being certainly more reliable for the approximate wave functions used. Particularly for large intermolecular distances, i.e. in the region of the Van der Waals minimum, the Hellmann–Feynman methods tends to underestimate the exchange forces. This must probably be assigned to the fact that the approximate monomer orbitals fall off too rapidly with increasing distance, and, therefore, undervalue the overlap effects on the electron density between the molecules. The Hellmann–Feynman forces originate directly from this electron density, which is probably the reason why they are more sensitive to the quality of the wave functions than the energy expectation values.

We are grateful to Roberto Gomperts for his assistance with the calculations. We thank Fred Mulder and Marc van Hemert for valuable discussions and for making available their unpublished results. Stimulating discussions with Dr. B. Jeziorski and with Professor R. McWeeny, who suggested the method to us, are gratefully acknowledged.

References


