Theoretical Modeling of Spectra and Collisional Processes of Weakly Interacting Complexes

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Abstract

The present status of symmetry-adapted perturbation theory applied to intermolecular potentials and interaction-induced properties is presented, and illustrated by means of applications to the calculations of the collision-induced Raman spectra, rovibrational spectra of weakly bound dimers, and second (pressure and dielectric) virial coefficients.

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1. Introduction

Over the last decades, there has been an increasing interest in theoretical (1, 2) and experimental (3) studies of weakly interacting complexes, the so-called van der Waals molecules. One of the reasons for this interest is that the spectra of these complexes depend very sensitively on the intermolecular potentials and other properties, such as interaction-induced dipole moments and polarizabilities, the knowledge of which is crucial for understanding the behavior of molecular bulk species.

Weakly bound complexes display unusual structural and dynamical properties resulting from the shape of their intermolecular potential energy surfaces. They show large amplitude internal motions, and do not conform to the dynamics and selection rules based on the harmonic oscillator/rigid rotor models (4). Consequently, conventional models used in the analysis of the spectroscopic data fail, and the knowledge of the full intermolecular potential and dipole/polarizability surfaces is essential to determine the assignments of the observed transitions.

The interaction-induced dipole moments and polarizabilities are also responsible for a wide range of dielectric, refractive, and optical properties of gases and fluids (5, 6). In pioneering studies Crawford et al. (7) and Chisholm and Welsh (8) have shown that during a collision of a helium atom with a hydrogen molecule the complex becomes temporarily infrared-active because of its relative translational motions, so that absorption and emission bands can be observed. Later, Levine and Birnbaum (9) predicted that all Raman spectra of gases should have a component caused by collision-induced changes in the polarizabilities, and it was first demonstrated by McTague and Birnbaum (10, 11) that colliding argon atoms undergo transitions between translational states when interacting with photons.

Despite the growing body of experimental work on bound state and collision-induced absorption and light scattering in weakly interacting complexes, not many full ab initio studies have been reported thus far. This is due, in part, to the enormous difficulty of obtaining an accurate ab initio description of the van der Waals bonding.

Recently, a new theoretical method of calculating potential energy and dipole/polarizability surfaces for van der Waals molecules based on symmetry-adapted perturbation theory (SAPT) of intermolecular forces (12)–(15) has been developed (16)–(24). In this method, referred to as many-body symmetry-adapted perturbation theory, all physically important contributions to the potential and the interaction-induced properties, such as electrostatics, exchange, induction, and dispersion are identified and computed separately. By making a perturbation expansion in the intermolecular interaction as well as in the intramolecular electronic correlation, it is possible to sum the correlation contributions to the different physical
effects only as far as necessary. The SAPT approach does not use the multipole expansion (24)–(29), so all charge penetration (damping) effects are automatically included. Since these various contributions show a different dependence on the intermolecular distance $R$, they can be fitted separately, with physically interpretable parameters.

In the present paper we review recent advances in the symmetry-adapted perturbation theory calculations of interaction potentials and interaction-induced properties. We will give a brief description of the theoretical methods needed on the route from the intermolecular potential and properties to rovibrational spectra and collision-induced Raman spectra. We also discuss applications of the interaction potentials and interaction-induced polarizabilities to compute (thermodynamic and dielectric) second virial coefficients. Finally, we illustrate these theoretical approaches on several examples from our own work.

2. Ab Initio Potential Energy Surfaces

The concept of an intermolecular potential appears in the Born-Oppenheimer approximation. The energy of interaction between molecules A and B is defined as,

$$E_{int} = E_{AB} - (E_A + E_B),$$

(1)

where $E_A$, $E_B$, and $E_{AB}$ are the exact ground-state energies of the monomers A and B, and of the dimer AB, and it is assumed that the internal coordinates of the monomers used in the calculations of $E_A$ and $E_B$ are the same as within the dimer AB.

Modern ab initio techniques used to calculate the interaction energy can be classified as supermolecular and perturbational. In a supermolecule approach the exact energies in Eq. (1) are replaced by approximations $\tilde{E}_{AB}$, $\tilde{E}_A$, and $\tilde{E}_B$ obtained from any of the available methods of solving the clamped-nuclei Schrödinger equation. The main drawback of this approach is that it does not permit an analysis of the interaction energy in terms of distinct, physically meaningful components, and it is not a priori obvious which contributions are neglected and which are included in a given supermolecular approach.

By contrast, the symmetry-adapted perturbation theory (1) defines the interaction energy directly, as the sum of polarization and exchange contributions,

$$E_{int} = E_{pol}^{(1)} + E_{exch}^{(1)} + E_{pol}^{(2)} + E_{exch}^{(2)} + \cdots,$$

(2)

where $E_{pol}^{(1)}$ is the classical electrostatic (Coulomb) energy calculated with full account of the penetration (overlap) of the charge distributions of the
monomers, $E_{\text{pol}}^{(2)}$ is the sum of the nonexpanded classical induction and quantum-mechanical dispersion energies,

$$E_{\text{pol}}^{(2)} = E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)}, \quad (3)$$

and $E_{\text{exch}}^{(n)}$, $n=1,2$, are the exchange components, which can be physically interpreted as an effect of the resonance tunneling of electrons between the interacting systems. The second-order exchange energy is also split into an induction and a dispersion part,

$$E_{\text{exch}}^{(2)} = E_{\text{exch-\text{ind}}}^{(2)} + E_{\text{exch-\text{disp}}}^{(2)}. \quad (4)$$

The exchange-induction energy $E_{\text{exch-\text{ind}}}^{(2)}$ and the exchange-dispersion energy $E_{\text{exch-\text{disp}}}^{(2)}$ can be viewed as a result of the coupling of the electron exchange with the induction and dispersion interactions.

Since the symmetry-adapted perturbation theory provides the basis for the understanding of weak intermolecular interactions, it is useful to discuss the convergence properties of the SAPT expansion. High-order calculations performed for model one-electron ($H_2^+$) (30), two-electron ($H_2$) (14, 15), and four-electron ($\text{He}_2$ and $\text{He}-\text{H}_2$) (31) systems show that the SAPT series converges rapidly. In fact, already the second-order calculation reproduces the exact variational interaction energies with errors smaller than 4%. Several recent applications strongly indicate that this optimistic result holds for larger systems as well.

In practical applications of the SAPT approach to interactions of many-electron systems, one has to use the many-body version of SAPT, which includes order-by-order the intramonomer correlation effects. The many-body SAPT is based on the partitioning of the total Hamiltonian as $H = F + V + W$, where the zeroth-order operator $F = F_A + F_B$ is the sum of the Fock operators for the monomers A and B. The intermolecular interaction operator $V = H - H_A - H_B$ is the difference between the Hamiltonians of interacting and noninteracting systems, and the intramonomer correlation operator $W = W_A + W_B$ is the sum of the Møller-Plesset fluctuation potentials of the monomers: $W_X = H_X - F_X$, $X = A$ or $B$. The interaction operator $V$ is taken in the non-expanded form, i.e., it is not approximated by the multipole expansion. The interaction energy components of Eq. (1) are now given in the form of a double perturbation series,

$$E_{\text{pol}}^{(n)} = \sum_{l=0}^{\infty} E_{\text{pol}}^{(nl)} \quad \text{and} \quad E_{\text{exch}}^{(n)} = \sum_{l=0}^{\infty} E_{\text{exch}}^{(nl)}, \quad (5)$$

where the superscripts $n$ and $l$ denote the orders of perturbation in $V$ and in $W$, respectively.
In practice, one has to truncate the expansions (5). Recent studies of the convergence of the many-body perturbation expansions of the electrostatic (18), exchange (19, 20), induction (21), and dispersion (22) energies led to the development of approximation schemes which can be used to compute these components with controlled accuracy. See Refs. (1, 23) for a detailed discussion of this point.

3. Ab Initio Interaction-Induced Properties

The interaction-induced dipole moment of a pair of molecules A and B is defined as the difference between the dipole moment of the complex AB and the sum of dipole moments of the noninteracting molecules A and B,

\[ \Delta \mu_i = \mu_i^{AB} - (\mu_i^A + \mu_i^B), \]

where \( \mu_i^{AB} \) is a Cartesian component of the dipole moment of the dimer AB, and \( \mu_i^A \) and \( \mu_i^B \) denote components of the dipole moments of the isolated molecules A and B. A similar definition holds for the interaction-induced polarizability of a pair of molecules A and B, i.e.,

\[ \Delta \alpha_{ij} = \alpha_{ij}^{AB} - (\alpha_{ij}^A + \alpha_{ij}^B), \]

where \( \alpha_{ij}^{AB} \) is a Cartesian component of the dimer polarizability tensor, and \( \alpha_{ij}^A \) and \( \alpha_{ij}^B \) denote components of the polarizability tensors of the isolated monomers A and B. By the use of the Hellmann-Feynman theorem Eqs. (6) and (7) can be conveniently rewritten as,

\[ \Delta \mu_i = -\left( \frac{\partial E_{\text{int}}}{\partial F_i} \right)_{F=0}, \]

\[ \Delta \alpha_{ij} = -\left( \frac{\partial^2 E_{\text{int}}}{\partial F_i \partial F_j} \right)_{F=0}, \]

where \( E_{\text{int}} \) is the interaction energy for the dimer in the presence of a static, uniform electric field \( F \).

Equations (2) and (8) define the SAPT expansions of the interaction-induced dipole moment and polarizability,

\[ \Delta \mu_i = \Delta \mu_{i,\text{pol}}^{(1)} + \Delta \mu_{i,\text{ezch}}^{(1)} + \Delta \mu_{i,\text{pol}}^{(2)} + \Delta \mu_{i,\text{ezch}}^{(2)} + \cdots, \]

\[ \Delta \alpha_{ij} = \Delta \alpha_{ij,\text{pol}}^{(1)} + \Delta \alpha_{ij,\text{ezch}}^{(1)} + \Delta \alpha_{ij,\text{pol}}^{(2)} + \Delta \alpha_{ij,\text{ezch}}^{(2)} + \cdots, \]

where the superscripts again indicate the order in the intermolecular interaction \( V \). Obviously an \( n \)th-order contribution to \( \Delta \mu_i \) or \( \Delta \alpha_{ij} \) is obtained by differentiating once or twice the corresponding energy contribution \( E_{\text{pol}}^{(n)} \) or \( E_{\text{ezch}}^{(n)} \), calculated when the system is placed in a (small) external electric field \( F \).
As discussed in Ref. (24), Eq. (9) relates the interaction-induced part of the dipole moment of the complex AB to the distortion of the electron density associated with the electrostatic, exchange, induction, and dispersion interactions of the monomers in the external field. For instance, the first-order multipole-expanded polarization contribution \( E_{pol}^{(1)} \) is due to the interactions of permanent multipole moments on A with moments induced on B by the external field \( F \), and vice versa. The terms linear in \( F \) give \( \Delta \mu_{i,pol}^{(1)} \).

The mechanism that yields the second-order induction dipole \( \Delta \mu_{i,\text{ind}}^{(2)} \) is more complicated, and one can distinguish two principal categories. The first mechanism is the interaction of a permanent multipole on monomer A with a multipole on B induced by the nonlinear (second-order) effect of both a permanent multipole on A and the external field \( F \) (plus a contribution obtained by interchanging the roles of the monomers A and B). The second mechanism is the interaction of a multipole moment on A, induced by a permanent multipole on B, with a moment on B induced by the field \( F \), and vice versa. Again, the energy terms linear in \( F \) give the corresponding induced dipoles. Finally, the dispersion term \( \Delta \mu_{i,\text{disp}}^{(2)} \) represents the intermonomer correlation contribution to the dipole moment of the dimer AB. The physical components to the interaction-induced polarizability can be classified analogously.

In practical applications of the SAPT approach to interaction-induced properties one has to use the many-body perturbation expansions discussed in the previous section. Thus, the physical contributions to \( \Delta \mu_i \) or \( \Delta \alpha_{ij} \) can be obtained by differentiating Eq. (5) once or twice.

Table 1
Comparison of the interaction-induced trace and anisotropy of the He\(_2\) polarizability computed by SAPT with the FCI results (in \( 10^{-3} \) a.u.).

<table>
<thead>
<tr>
<th></th>
<th>( R = 3 ) bohr</th>
<th>( R = 4 ) bohr</th>
<th>( R = 5 ) bohr</th>
<th>( R = 8 ) bohr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAPT</td>
<td>124.034</td>
<td>75.693</td>
<td>110.519</td>
<td>78.365</td>
</tr>
<tr>
<td>FCI</td>
<td>133.327</td>
<td>71.826</td>
<td>111.912</td>
<td>79.766</td>
</tr>
</tbody>
</table>

Recently, the convergence of the many-body SAPT expansion for the interaction-induced dipole moment of He–H\(_2\) (24) and the polarizability of He\(_2\) (24, 32). has been checked by comparison with FCI results in the same basis set. The numerical results for the helium dimer are summarized in Table 1 where we consider the anisotropy \( \gamma \) and the trace \( \alpha: \gamma = \Delta \alpha_{zz} - \Delta \alpha_{xx} \) and \( \alpha = (\Delta \alpha_{zz} + 2\Delta \alpha_{xx})/3 \), in which the \( z \)-axis is the molecular axis. An inspection of Table 1 shows that for all distances considered in Ref. (32) the many-body SAPT expansion reproduces the FCI results to
within 3%. Similar results for the interaction-induced dipole moment of He-H$_2$ have been reported in Ref. (24). Hence, the convergence of the many-body SAPT series for the interaction-induced electrical properties appears to be satisfactory, at least for simple four-electron dimers.

4. Applications

A. Collision-Induced Light Scattering in Helium Gas

In collision-induced Raman experiments laser light of wavenumber $\omega_0$ is scattered inelastically by the interacting atoms in the gas. The intensities of the depolarized and polarized scattered light are given by (33, 34),

$$D(\nu) = \frac{2}{15} \omega^3 \omega_0 G(\nu), \quad P(\nu) = \omega^3 \omega_0 A(\nu),$$

where $\nu$ is the frequency shift, $\omega = \omega_0 - 2\pi \nu/c$, and $c$ is the speed of light. The spectral functions $G(\nu)$ and $A(\nu)$ can be written as,

$$G(\nu) = \frac{2hc\lambda_B^3}{(2I + 1)^2} \sum_{J,J'} g_J(2J + 1) \int_0^{\infty} dE e^{-E/k_BT} b_{J'}^J |\langle E', J' | \gamma(R) | E, J \rangle|^2,$$

$$A(\nu) = \frac{2hc\lambda_B^3}{(2I + 1)^2} \sum_J g_J(2J + 1) \int_0^{\infty} dE e^{-E/k_BT} |\langle E', J | \alpha(R) | E, J \rangle|^2,$$

where $E' - E = h\nu$, $J' = J, J \pm 2$, $h$ is the Planck constant, $k_B$ is the Boltzmann constant, $T$ denotes the temperature, $\lambda_B = (h^2/2\pi \mu k_B T)^{1/2}$ is the de Broglie wavelength, $\mu$ is the reduced mass of the collisional complex, and $I$ and $g_J$ designate the nuclear spin and nuclear spin statistical weight, respectively. The constants $b_{J'}^J$ are given by Eqs. (12)–(14) of Ref. (34) and the matrix elements of the trace and anisotropy of the polarizability appearing in Eqs. (12) and (13) are defined as,

$$\langle E', J' | X(R) | E, J \rangle = \int_0^{\infty} \psi_{E'J'}^*(R) X(R) \psi_{EJ}(R) dR,$$

where the scattering wave functions $\psi_{EJ}(R)$ are solutions of the radial Schrödinger equation describing the relative motion of the atoms in the potential $V(R)$, subject to the energy normalization condition.

The collision-induced light scattering in the helium gas has been subject of many experimental studies (35)–(42). Most of these measurements were done at high densities (35)–(37), so the reported Raman intensities were affected by three-body contributions, and pure pair spectra had to be separated out (37) by applying simplified models. Only the polarized
Figure 1
Comparison of the theoretical (solid lines) and experimental (circles and error bars) depolarized spectra (a), and polarized spectra (b), for the ⁴He diatom.

and depolarized Raman spectra reported by Proffitt, Keto, and Frommhold (41, 42) were shown to be free from three-body contributions.

These experimental advances stimulated associated theoretical developments. In an extensive theoretical study Dacre and Frommhold (43) have checked the accuracy of the \textit{ab initio} CISD (CISD stands for the Configuration Interaction method restricted to single and double substitutions) trace and anisotropy polarizabilities of He₂ (44) by exposing them to the test of computing the observed Raman intensities. While the depolarized spectra computed from Dacre’s polarizability (44) showed good agreement with the experiment, the theoretical polarized spectrum was much less intense than the spectrum derived from the experiment (43).

The reasons for the less satisfactory agreement between the theoretical and experimental polarized Raman spectra may be both on the theoretical and on the experimental sides. The experimental polarized spectrum is obtained as the difference of two nearly equal signals excited with different beam polarizations (41, 42), and the accuracy of the polarized intensities deduced from the experiment is rather poor. On the other hand, the theoretical values of the interaction-induced trace may suffer from the size-inconsistency of the CISD method or from the basis set superposition error.

Recently, the SAPT approach has been applied (32) to compute the interaction-induced polarizability for the helium diatom. The computed polarizability invariants have been analytically fitted, and used in quantum-dynamical calculations of the binary collision-induced Raman spectra. The results of the dynamical calculations are summarized in Fig. 1.

An inspection of Fig. 1 shows that the agreement of the theoretical and
measured (42) depolarized Raman intensities is satisfactory. Most of the intensities agree within 3% or better. Only at very low and high frequency shifts this good agreement deteriorates somewhat. Still, the predicted intensities at high frequencies are within the experimental error bars. At very low frequencies the theoretical results are outside the experimental error bars, but these discrepancies are consistent with the estimated (combined) error of the SAPT and dynamical calculations.

The theoretical polarized Raman intensities agree with the experiment within the large (±50% — 60%) experimental error bars over a wide range of the frequency shifts. Except for the low frequency region, the predicted polarized spectrum is much less intense. It is worth noting that our results for the depolarized and polarized Raman intensities are in good agreement with those generated from the CISD polarizability invariants (43). Both these observations suggest that the theoretical results are rather well converged, and that the error in the \textit{ab initio} polarized intensities is considerably smaller than the experimental error of 50 to 60%. Hence, the improvement of the agreement between theory and experiment for these intensities should mainly come from the experimental side.

B. Second Dielectric Virial Coefficient of Helium Gas

It is well known that for atomic gases at low densities the Clausius-Mossotti function can be related to the atomic polarizability via the relation:

\[
\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\alpha_0}{3}\rho,
\]

where \(\epsilon\) is the dielectric constant, \(\alpha_0\) is the atomic polarizability, and \(\rho\) denotes the gas number density. At higher pressures deviations from this relation are observed, and they can be attributed to intermolecular interactions. Buckingham and Pople (45) have shown that the leading correction to Eq. (15), quadratic in the gas density, is given by \(B_\epsilon(T)\rho^2\), where the second dielectric virial coefficient \(B_\epsilon(T)\) is related to the interatomic potential and interaction-induced polarizability trace by,

\[
B_\epsilon(T) = \frac{2\pi}{3} \int_0^\infty \alpha(R) \exp(-V(R)/k_BT)R^2 dR.
\]

At very low temperatures Eq. (16) is no longer valid, and one has to use the exact quantum-statistical expression. The quantum equivalent of Eq. (16) has been recently developed in Ref. (46). Its derivation starts with the general relation between the second dielectric virial coefficient and the ordinary (pressure) second virial coefficient of an atomic gas in a uniform
electric field (46),

\[ B_\varepsilon(T) = -\frac{4\pi k_B T}{3} \left( \frac{\partial^2 B_2(T; F)}{\partial F^2} \right) \bigg|_{F=0}, \tag{17} \]

where \( B_2(T; F) \) denotes the ordinary (pressure) second virial coefficient for the gas in the electric field \( F \). Using Eq. (17) and an expression for \( B_2(T; F) \) in terms of the field-dependent Slater sum (47), one finds the following formula for \( B_\varepsilon(T) \),

\[
B_\varepsilon(T) = \frac{2\pi \lambda_B^3}{3} \sum_{J=0}^{\infty} (2J + 1) \left[ 1 + \frac{(-1)^{J+2I}}{2I+1} \right] \\
\times \left[ \sum_{n} e^{-E_{nJ}/k_BT} \langle n, J | \alpha(R) | n, J \rangle \\
+ \frac{2}{\pi} \int_0^{\infty} e^{-\hbar^2 k^2/2\mu k_BT} \langle E, J | \alpha(R) | E, J \rangle dk \right], \tag{18} \]

where

\[ \langle n, J | \alpha(R) | n, J \rangle \equiv \int_0^{\infty} \psi_{nJ}^*(R) \alpha(R) \psi_{nJ}(R) dR, \tag{19} \]

\( |n, J) = \psi_{nJ}(R) \) denote the bound-state eigenfunctions of the Schrödinger equation for the relative motion in the potential \( V(R) \), with eigenvalues \( E_{nJ} \), and \( |E, J) \) are the scattering states with energies \( E = \hbar^2 k^2/2\mu \) defined above.

Equation (17) can also be used to derive the semiclassical expansion of the second dielectric virial coefficient. Indeed, one may hope that at intermediate temperatures an expansion of \( B_\varepsilon(T) \) as a power series in \( \hbar^2 \) will give sufficiently accurate results, making full quantum-statistical calculations unnecessary. Thus, one can approximate \( B_\varepsilon(T) \) as,

\[ B_\varepsilon(T) = B_\varepsilon^{(0)}(T) + B_\varepsilon^{(1)}(T) + B_\varepsilon^{(2)}(T), \tag{20} \]

where the classical term \( B_\varepsilon^{(0)}(T) \) is given by the r.h.s. of Eq. (16), while the quantum corrections of the order \( \hbar^2 \) and \( \hbar^4 \) (denoted by \( B_\varepsilon^{(1)}(T) \) and \( B_\varepsilon^{(2)}(T) \), respectively), can be written as (32),

\[
B_\varepsilon^{(1)}(T) = -\frac{\pi^2 \hbar^2}{9\mu k_B^2 T^2} \int_0^{\infty} \exp(-V(R)/k_BT) \\
\times \left[ \frac{\alpha(R)}{k_BT} \left( \frac{dV}{dR} \right)^2 - 2 \frac{dV}{dR} \frac{d\alpha}{dR} \right] R^2 dR, \tag{21} \]

\[
B_\varepsilon^{(2)}(T) = \frac{\pi^2 \hbar^4}{180\mu^2 k_B^3 T^3} \int_0^{\infty} \exp(-V(R)/k_BT) \left[ \frac{\alpha(R)}{k_BT} f(R) + g(R) \right] R^2 dR, \tag{22} \]
Table 2
Second dielectric virial coefficient of $^4$He (in cm$^6$/mol$^{-2}$) as function of the temperature (in K).

<table>
<thead>
<tr>
<th>$T$</th>
<th>$B_e^{(0)}(T)$</th>
<th>$B_e^{(1)}(T)$</th>
<th>$B_e^{(2)}(T)$</th>
<th>$B_e(T)^a$</th>
<th>$B_e(T)^b$</th>
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<tr>
<td>5</td>
<td>-0.0512</td>
<td>0.3040</td>
<td>-2.0226</td>
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</tr>
<tr>
<td>7</td>
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<td>0.1028</td>
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<td>-0.0085</td>
</tr>
<tr>
<td>10</td>
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<td>0.0403</td>
<td>-0.1088</td>
<td>-0.0894</td>
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</tr>
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<td>20</td>
<td>-0.00170</td>
<td>0.0100</td>
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<tr>
<td>30</td>
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<td>-0.0446</td>
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</tr>
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</table>

$^a$Semiclassical approximation through the second-order.
$^b$Exact quantum-statistical calculation.

where the functions $f(R)$ and $g(R)$ are given by Eqs. (35)–(36) of Ref. (32).

Recently, a detailed study of the importance of the quantum effects and of the applicability of the semiclassical expansion has been reported (46). This study started from the ab initio SAPT trace polarizability (32) and it involved semiclassical and full quantum calculations of the second dielectric virial coefficient for the $^4$He gas at various temperatures. Illustrative results of these calculations are presented in Table 2.

An inspection of Table 2 shows that the quantum effects are small for temperatures larger than 100 K, and $B_e(T)$ can be approximated by the classical expression with an error smaller than 2.5%. At lower temperatures the dielectric virial coefficient of $^4$He starts to deviate from the classical value. Still, for $T \geq 50$ K the quantum effects can be efficiently accounted for by the sum of the first and second quantum corrections. Indeed, for $T = 50, 75,$ and 100 K the series $B_e^{(0)}(T) + B_e^{(1)}(T) + B_e^{(2)}(T)$ reproduces the exact results with errors smaller than 2%. Only at temperatures below 50 K the semiclassical expansion of the second dielectric virial coefficient in powers of $\hbar^2$ starts to diverge, and full quantum calculations are needed.

The dielectric properties of helium gas are of great experimental interest, and it is not surprising that since the early 1960's increasingly accurate measurements (48)–(57) are reported in the literature. The comparison of the theoretical and experimental values of the second dielectric virial coefficient can serve as a further check of the accuracy of the ab initio trace polarizability. An example of such a comparison is shown on Fig. 2, where
Figure 2
Comparison of the \textit{ab initio} and experimental second dielectric virial coefficients of $^4$He at various temperatures. The solid line represents the second dielectric virial coefficients generated from the \textit{ab initio} polarizability trace of Ref. (32), and the empirical potential of Ref. (58). Crosses label the indirect measurements from Refs. (51, 55, 56, 57), open circles and squares the measurements from Refs. (54), and (49), respectively, and filled circles and squares represent experimental data from Refs. (50) and (52, 53).

The theoretical and experimental second dielectric virial coefficients for the $^4$He gas at various temperatures are reported. The \textit{ab initio} data have been generated (46) from the \textit{SAPT} trace polarizability of He$_2$ (32).

At high temperatures the \textit{ab initio} results agree well with the data from indirect measurements (51, 55, 56, 57). The only exception is the value at $T = 242.95$ K. Here the theoretical result is slightly outside the experimental error bars. The agreement with the results of direct measurements (49, 50, 52, 53, 54) is less satisfactory. The \textit{ab initio} results agree very well with the old experimental data of Orcutt and Cole (49), and disagree with the data of Vidal and Lallemand (52, 53). Since the theoretical values agree with the majority of the high-temperature experimental data, and since the second dielectric virial coefficient changes very slowly with temperature, it is very likely that the results of direct measurements reported by Vidal and Lallemand (53) are contaminated by nonadditive three-body effects.

At low temperatures the situation is more complex. The \textit{ab initio} result at 77.4 K agrees very well with the value from indirect measurements re-
ported by Huot and Bose (56). Other low temperature data were obtained from direct measurements (54) and show much scatter. At T = 13.804 K the \textit{ab initio} value agrees with the measurement, while at T = 7.198 K the theoretical result is almost within the experimental error bars. At other temperatures the disagreement is quite substantial, and it is unlikely that the theoretical polarizability trace will change so drastically. Therefore, these data should probably be remeasured.

C. Rovibrational Spectra of Weakly Bound Complexes: He–CO and He–HF

Depending on the strength of the anisotropy in the interaction potential, nuclear motions in weakly bound van der Waals complexes are usually described using a set of coordinates related to a space-fixed or body-fixed frame (2). When the anisotropy of the potential in the region of the van der Waals minimum is relatively weak one can expect that the diatomic molecule in the complex should behave as a nearly free rotor, \textit{i.e.}, that the space-fixed description is appropriate. As a consequence, the energy levels and infrared transitions can be approximately classified by the use of the case \textit{a} coupling of Bratoz and Martin (59) (see Refs. (2, 60) for a review). Moreover, the intramolecular vibrations can, to a good approximation, be decoupled from the intermolecular modes due to their high frequency, and vibrationally averaged rotational constants $b_v$ of the diatom can be used. Thus, we have the following Hamiltonian describing the nuclear motion,

$$H = -\frac{\hbar^2}{2\mu R^*} \frac{\partial^2}{\partial R^2} R + \frac{l^2}{2\mu R^2} + b_v j^2 + V,$$

where $\mu$ is the reduced mass of the dimer, $j$ is the angular momentum of the diatom, and $l$ denotes the angular momentum associated with the end-over-end rotation of the complex.

In the limit of vanishing anisotropy the quantum numbers $j$, which describes the rotation of the diatom in the dimer, and $l$, which corresponds to the rotation of the vector $R$ are good quantum numbers. The total angular momentum $J = j + l$ is always conserved, due to the isotropy of space, but $j$ and $l$ are broken by the anisotropy in the potential. A degenerate $(j, l)$-level splits into sublevels $J = |j - l|, \ldots, j + l$ under the influence of the anisotropy. If these splittings are small, like in the Ar–H$_2$ (61) and He–C$_2$H$_2$ (62) cases, the states can still be labeled to a good approximation by $j$ and $l$.

The wave function $\Psi^{JM}(R, \hat{R}, \hat{\tau})$ can be expanded in a basis of products of radial functions $\chi_n(R)$ and angular functions which are Clebsch-Gordan
coupled spherical harmonics,
\[ [Y^j(\hat{\mathbf{r}}) \otimes Y^l(\hat{\mathbf{R}})]_M^J = \sum_{m_i,m_j} \langle jm_j; lm_i|JM \rangle Y^j_{m_j}(\hat{\mathbf{r}}) Y^l_{m_i}(\hat{\mathbf{R}}), \]

where \(Y^j_m\) denotes the normalized spherical harmonics, \(\langle jm_1; jm_2|JM \rangle\) is the Clebsch-Gordan coefficient (63), \(\hat{\mathbf{R}}\) stands for the spherical polar angles of \(\mathbf{R}\) with respect to a space-fixed frame and an analogous definition holds for \(\hat{\mathbf{r}}\). The angular basis functions have a well defined parity \(p = (-1)^{j+l}\), so the full Hamiltonian, Eq. (23), is blocked in both \(p\) and \(J\). Within each block various \(j\) and \(l\) are mixed through the potential.

The infrared transitions in the atom–diatom complexes will obey the following selection rules: \(|\Delta p| = 1\), and \(|\Delta J| = 1\) or 0. Additionally, if the energy levels can be labeled with the quantum numbers \(j\) and \(l\), the selection rules \(\Delta l = 0\) and \(|\Delta j| = 1\) should hold approximately.

When the leading anisotropic term is large compared to the rotational constant of the complex, and small compared with the rotational constant of the free diatom, the energy levels and infrared transitions can be approximately classified using the case \(b\) coupling of Bratoz and Martin (59), i.e., the diatom in the complex should behave as a hindered rotor. Choosing the embedded reference frame such that the vector \(\mathbf{R}\) connecting the diatom center of mass with the atom defines the new \(z\) axis, the Hamiltonian describing the nuclear motion can be written as (64)–(66),
\[ H = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\mathbf{J}^2 + j^2 - 2j \cdot \mathbf{J}}{2\mu R^2} + b_\sigma j^2 + V. \]

Here, the operator \(\mathbf{j}\) acts on the angular coordinates of the vector \(\mathbf{r}\) in the body-fixed frame. Note, that the present coordinate system corresponds to the so-called “two-thirds body-fixed” system of Refs. (2, 66). Therefore, the angular momentum operator \(\mathbf{j}\) and the pseudo angular momentum operator \(\mathbf{J}\) do not commute, so the second term in Eq. (25) cannot be factorized.

The only rigorously conserved quantum numbers are, again, the total angular momentum \(J\) and the spectroscopic parity \(\sigma\). [The spectroscopic parity \(\sigma\) is related to the conventional parity \(p\) by the relation \(\sigma = p(-1)^J\).] The diatom rotational quantum number \(j\), and the projection \(K\) of \(\mathbf{J}\) (or \(\mathbf{j}\)) onto the intermolecular axis, are only approximately conserved. This conservation is broken by off-diagonal Coriolis interaction. Since \(K\) is the projection of an angular momentum, states with \(K = 0, \pm 1,\) etc., are denoted as \(\Sigma, \Pi,\) etc.. In addition, levels with \(\sigma = +1\) and \(\sigma = -1\) will be designated by superscripts \(e\) and \(f\), respectively. For \(K = 0\) only \(e\) parity states exist. The case \(b\) coupling of Bratoz and Martin (59) gives a very simple classification of the rovibrational energy levels of the complex: each monomer rotational level \(j\) is split into \(j + 1\) levels corresponding to any
\( J \geq |K| \) with \( K = 0, \pm 1, \pm 2, \ldots, \pm j \). The inclusion of the Coriolis interaction introduces further splitting of the states with \( |K| \neq 0 \) (the so-called \( l \)-doubling) into states with \( e \) and \( f \) parity labels.

The wave function describing the nuclear motion can be expanded in a basis of products of radial functions \( \chi_n(R) \) and angular functions of the form,

\[
[Y^j_K(\theta, \varphi)D^{(J)*}_{M,K}(\alpha, \beta, 0) + \sigma Y^{-j}_K(\theta, \varphi)D^{(J)*}_{M,-K}(\alpha, \beta, 0)]
\]

where \((\beta, \alpha)\) are polar angles of the \( R \) vector in the space-fixed coordinates, \( \theta \) and \( \varphi \) are the spherical angles of the \( r \) vector in the body-fixed coordinates, and \( D^{(J)}_{M,K}(\alpha, \beta, \gamma) \) is an element of the Wigner rotation matrix (63). The angular basis functions have a well defined parity \( \sigma \), so the full Hamiltonian, Eq. (25), is blocked in both \( \sigma \) and \( J \). Within each block functions with different \( K \) are mixed through the off-diagonal Coriolis interaction.

The allowed dipole transitions between the states of the complex can be deduced from an analysis of the expression for the transition intensity, and it follows easily that the observed dipole transitions must obey the following rigorous selection rules: \(|\Delta J| = 1, \Delta \sigma = 0 \) or \( \Delta J = 0, |\Delta \sigma| = 2 \). Since the \( K \) quantum number is nearly conserved, an additional approximate selection rule should hold: \(|\Delta K| = 0, 1 \).

The wave functions for the initial and final states obtained by solving the Schrödinger equation with the Hamiltonian of Eq. (23) or (25) can be used to compute the infrared absorption intensities for the complex. The infrared absorption coefficient \( I(J'' \rightarrow J') \) for the transition \( J'' \rightarrow J' \) is proportional to,

\[
\frac{\exp(-E_{J''}/k_BT)}{Z(T)} \frac{E_{J'} - E_{J''}}{S(J'' \rightarrow J')},
\]

where \( E_J \) denotes the energy of the state labeled by \( J \), \( Z(T) \) is the partition function, the line strength is given by,

\[
S(J'' \rightarrow J') = \sum_{M'', M', m} \left| \langle \Psi^J'M' | \mu_m | \Psi^{J''}M'' \rangle \right|^2,
\]

and \( \mu_m \) is the spherical component of the dipole moment of the dimer (for the far-infrared transitions) or the spherical component of the transition dipole (for the near-infrared transitions).

He–CO and He–HF complexes are very suitable systems to verify how well the theory that goes all the way from \textit{ab initio} calculations of the intermolecular potentials to line positions and intensities can reproduce the experimentally observed spectra. For both systems high-resolution infrared spectra have been recorded (67, 68). In addition, for He–HF also the rotational predissociation line widths have been measured (68).
Figure 3
Comparison of theoretical and experimental infrared spectra of the $^4$He–CO complex (a), and $^3$He–CO (b) complex, accompanying the fundamental band of CO. The temperature is 50 K.

Recently, SAPT and dynamical calculations for the He–CO complex have been reported (69). Although the anisotropy of the interaction potential around the van der Waals minimum is not particularly weak, we followed Ref. (67) and described the nuclear dynamics in the space-fixed coordinates. The computed infrared spectra for the $^4$He–CO and $^3$He–CO complexes are presented in Fig. 3.

An inspection of Fig. 3 shows that the agreement of theoretical transition frequencies and intensities with the results of high-resolution measurements (67) is satisfactory. Most of the line positions agree within 0.1–0.2 cm$^{-1}$ or better. The intensities are also accurately predicted by the ab initio potential. However, some transition frequencies are in error by $\sim 0.5$ cm$^{-1}$, suggesting that the anisotropy of the ab initio potential is not entirely correct. The reason for this small disagreement has been traced (69) to the neglect of higher-order contributions (in the intramonomer correlation) to the exchange-repulsion energy. Bound state calculations using a scaled potential (in which the contribution of the short-range energy to the second Legendre component was increased by 4.5%) gave a spectrum in much better agreement with the experiment. It is worth noting that this scaling is consistent with the estimated effect of the higher-order correlations on the first-order exchange energy.

A similar application has been recently reported for the He–HF system
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(70, 71). Starting from the ab initio SAPT potential energy surface for this system (70) the authors of Ref. (71) performed converged variational calculations of the energy levels and transition frequencies in the near-infrared spectrum of He–HF accompanying the fundamental band of HF. Although the anisotropy of the interaction potential at the van der Waals minimum is not particularly strong, the body-fixed description of the nuclear motion was found to be the most appropriate. In Table 3 the computed transition frequencies are compared with the measured values (68).

Table 3
Near-infrared transitions in He–HF (in cm⁻¹) accompanying the fundamental band of HF.

<table>
<thead>
<tr>
<th>transition</th>
<th>J''</th>
<th>J'</th>
<th>∆E(J'' → J')</th>
<th>∆E(J'' → J')</th>
<th>Δa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ → Σ°</td>
<td>0</td>
<td>1</td>
<td>3999.860</td>
<td>3999.953</td>
<td>−0.094</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>4000.044</td>
<td>4000.137</td>
<td>−0.093</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4000.164</td>
<td>4000.251</td>
<td>−0.087</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>4000.266</td>
<td>4000.345</td>
<td>−0.079</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>4000.378</td>
<td>4000.449</td>
<td>−0.071</td>
</tr>
<tr>
<td>Σ → Π°</td>
<td>0</td>
<td>1</td>
<td>4003.102</td>
<td>4003.161</td>
<td>−0.059</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>4004.402</td>
<td>4004.418</td>
<td>−0.016</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3</td>
<td>4000.806</td>
<td>4000.904</td>
<td>−0.098</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4</td>
<td>4000.655</td>
<td>4000.735</td>
<td>−0.080</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5</td>
<td>4000.583</td>
<td>4000.639</td>
<td>−0.056</td>
</tr>
<tr>
<td>Σ → Π’</td>
<td>1</td>
<td>1</td>
<td>4001.916</td>
<td>4002.005</td>
<td>−0.089</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>4001.871</td>
<td>4001.952</td>
<td>−0.081</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3</td>
<td>4001.796</td>
<td>4001.859</td>
<td>−0.063</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>4001.669</td>
<td>4001.680</td>
<td>−0.011</td>
</tr>
</tbody>
</table>

Δa: Absolute error of the transition frequency computed from the ab initio potential (70).

The agreement of theoretical transition frequencies with the results of high-resolution measurements (68) is excellent. The ab initio potential energy surface predicts all infrared transitions with errors smaller than 0.1 cm⁻¹. In particular, the band origins of the computed and measured near-infrared spectra agree within 0.2% or better. It follows from the case b coupling of Bratoz and Martin (59) that the transition energies are mainly sensitive to even terms in the Legendre expansion of the potential. The results reported in Table 3 show that at least even terms in the SAPT potential are very accurate.

The correctness of the small odd terms has been checked by computing the rotational predissociation line widths. Rotational predissociation life-
times can be obtained from the Fermi golden rule expression (72) which shows that the mixing of states with \( j = 0 \) and \( j = 1 \) occurs mainly via the first Legendre component of the potential. In Ref. (71) the widths of the resonances that correspond to rotational predissociation were directly obtained from close-coupling calculations. In Table 4 the widths of the \( \Sigma^e \) and \( \Pi^e \) resonances calculated from the \textit{ab initio} potential (70) are compared with the experimental results (68).

### Table 4
Calculated widths (MHz) of the \( \text{HeHF} \) resonance states. The widths corresponding to the scaled potential are given in parentheses.

<table>
<thead>
<tr>
<th>( J )</th>
<th>( \Gamma_j )</th>
<th>( \Gamma_j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. (71)</td>
<td>observed (68)</td>
<td></td>
</tr>
<tr>
<td>( \Sigma^e ) bend</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7203 (3452)</td>
<td>3020 ± 500</td>
</tr>
<tr>
<td>2</td>
<td>5731 (2673)</td>
<td>2830 ± 200</td>
</tr>
<tr>
<td>3</td>
<td>4453 (2001)</td>
<td>1640 ± 150</td>
</tr>
<tr>
<td>4</td>
<td>3280 (1397)</td>
<td>1260 ± 100</td>
</tr>
<tr>
<td>5</td>
<td>2158 (848)</td>
<td>770 ± 100</td>
</tr>
<tr>
<td>( \Pi^e ) bend</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1080 (575)</td>
<td>530 ± 100</td>
</tr>
<tr>
<td>2</td>
<td>1773 (928)</td>
<td>890 ± 150</td>
</tr>
<tr>
<td>3</td>
<td>1930 (993)</td>
<td>1000 ± 400</td>
</tr>
</tbody>
</table>

The agreement here is less satisfactory: all computed widths are a factor of two larger than the measured line widths (68). This suggests that the small \( P_1 (\cos \theta) \) anisotropy of the potential is not correct. To confirm this assumption the widths of the \( \Sigma^e \) and \( \Pi^e \) resonances were recomputed using a potential in which the contribution of the short-range energy to this first Legendre component was scaled by 0.95. The resulting widths are given in parentheses. The agreement with the measured line widths is very good: almost all widths computed using the scaled potential agree with the experimental data within the experimental error bars. It should be noted that this 5% scaling of the short-range \( P_1 (\cos \theta) \) term introduces only a very small change in the interaction potential. In the repulsive region \(( R = 5 \text{ bohr and } \theta = 0^\circ)\) the scaled potential is \( \approx 4\% \) smaller than the \textit{ab initio} potential, while the depth of the van der Waals well is only 2\% lower. This confirms that the overall anisotropy of the \textit{ab initio} potential is correct. Small inaccuracies of the order of 2\% may be due to basis set unsaturation of the exchange-repulsion contribution.

#### D. Excess Second Virial Coefficients for \( \text{He–CO} \)
Additional information about the accuracy of the theoretical interaction potentials can be obtained by comparison of the measured and computed
Comparison of the \textit{ab initio} and experimental second virial coefficients. The solid and dashed lines represent second virial coefficients generated from the original and scaled \textit{ab initio} potentials, respectively, while the dotted line shows the second virial coefficient calculated using the isotropic component of the \textit{ab initio} potential. Circles and squares are experimental points from Refs. (74) and (73), respectively.

excess second virial coefficients. The \textit{ab initio} potential energy surface for He–CO (69) has been checked by computing the second virial coefficient $B(T)$ over the temperature range in which it has been measured (73, 74). We used directly the formulas for atom-linear molecule derived by Pack (75). Specifically, we have computed the classical term, $B^{(0)}(T)$, and included the first quantum corrections due to relative translational motions, $B^{(1)}_R(T)$, to molecular rotations, $B^{(1)}_A(T)$, and to the Coriolis term, $B^{(1)}_C(T)$:

$$B(T) = B^{(0)}(T) + B^{(1)}_R(T) + B^{(1)}_A(T) + B^{(1)}_C(T).$$

The results of these calculations are presented in Fig. 4.

An inspection of Fig. 4 shows that the \textit{ab initio} results agree well with the experimental data of Schramm and collaborators (73, 74). Only at the two lowest temperatures this good agreement deteriorates somewhat, and the present results are just outside the error bars of the new measurements (74), but within the (larger) error bars of the previous experimental data (73). However, at low temperatures the quantum corrections become rather significant, so higher corrections may be important. Especially, the second ($O(\hbar^4)$) radial correction may be nonnegligible. Also presented in Fig. 4 is the second virial coefficient computed using the scaled \textit{ab initio} potential
(cf. previous section). This scaling has a negligible effect on the computed second virial coefficients. Finally, it is worth noting that the effect of the anisotropy in the potential is relatively important (see Fig. 4). Except for the high temperature region, the neglect of the anisotropic terms in the potential would lead to second virial coefficients outside the experimental error bars.

5. Summary and Conclusions

In this paper we have given a short overview of the application of symmetry-adapted perturbation theory to intermolecular potentials and interaction-induced properties, and of the methods going directly from these intermolecular properties to experimentally measurable quantities such as collision-induced Raman spectra, rovibrational spectra, and second (pressure and dielectric) virial coefficients. The results presented in this paper show that intermolecular potentials and dipole/polarizability surfaces obtained from ab initio SAPT calculations can be used to correctly describe the spectroscopic and dynamical processes involving weakly bound complexes.

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