Molecular Structure and Molecular Collisions

Les Houches, 2005

But see Sheldon Green, Les Houches 1974

Interactions between atoms: molecular potentials

molecular structure

molecular collisions

Examples: H_2 (the simplest molecule), i.e. H+H

$H - H_2$ (the 'simplest' collision system)

We shall use: classical mechanics for insight

quantum mechanics for calculations, specifically the non-relativistic Schrödinger equation

The simplest atom-atom system : H + H

Of great importance in the interstellar medium (ISM) and the Universe in general, where H_2 is by far the most abundant molecule.

Consider the time-independent Schrödinger equation:

$$(H - E) \, \Psi = 0$$

H is hamiltonian

E is total energy

Ψ is wave function

We write $\quad H = T + V$

T is kinetic energy (operator)

V is potential energy

H + H system consists of 2 protons and 2 electrons

$$T = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{2} \vec{\nabla}_i^2 \, (x_i, y_i, z_i)$$

$$-\frac{\hbar^2}{2m_p} \sum_{j=1}^{2} \vec{\nabla}_j^2 \, (X_j, Y_j, Z_j)$$

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In cartesian coordinates, the Laplacian operator is

$$\vec{\nabla}^2 (x, y, z) \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In practice, coordinates other than cartesian (spherical polar, cylindrical, spheroidal) may be used (and often are used).

Let $\vec{r} \equiv (x, y, z)$ and $\vec{R} \equiv (X, Y, Z)$

Then

$$V = \frac{e^2}{|\vec{R}_1 - \vec{R}_2|} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$
$$- \frac{e^2}{|\vec{R}_1 - \vec{r}_1|} - \frac{e^2}{|\vec{R}_1 - \vec{r}_2|}$$
$$- \frac{e^2}{|\vec{R}_2 - \vec{r}_1|} - \frac{e^2}{|\vec{R}_2 - \vec{r}_2|}$$

[sum of the Coulomb interactions between the (charged) constituents of the two atoms]

(3)

The Schrödinger equation is a second order, homogeneous differential equation. The H - H system is a 12 - dimensional promblem (4×3) :

$$\Psi = \Psi (\vec{r_1}, \vec{r_2}, \vec{R_1}, \vec{R_2})$$

Even in 2005, one hesitates to use brute-force numerical methods to solve this Schrödinger equation; more subtle techniques are advisable.

The Born - Oppenheimer approximation is still

central to studies of molecular interactions, even though it was introduced in the early years of quantum mechanics.

Any ensemble of freely - interacting particles will tend towards equipartition of energy and minimization of their total energy. Whilst the Coulomb interactions are independent of the particle masses, their kinetic energies ($\frac{1}{2} m v^2$) are mass-dependent.
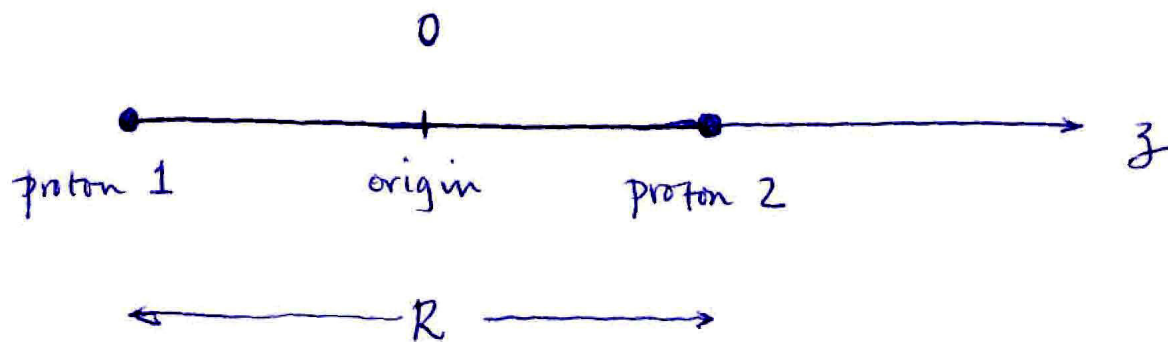
The proton : electron mass ratio $m_p / m_e \approx 1836$.

Thus, for the same kinetic energy, the electron speed is approximately 43 times larger than the proton speed.

It follows that it is often a good approximation (the 'B-O approximation) to consider that, for any given set of nuclear coordinates, the electrons (i.e. the electron probability distribution and wave functions) adapt so as to *minimize the total energy of the system*. Thus, in the example of H + H, the protons are considered to be fixed and the electrons as moving.

If the nuclei are considered fixed, the coordinate system may be chosen such that the z-axis coincides with the internuclear axis, with the coordinate origin at the mid-point:

Then, the only coordinate which is required to locate the protons is the internuclear distance, R.

Furthermore, the kinetic energy of the protons drops out of the Schrödinger equation and the proton–proton Coulomb repulsion is constant. Only the electron interactions with the (fixed) protons and their mutual repulsion, together with their kinetic energy, need to be taken into account:
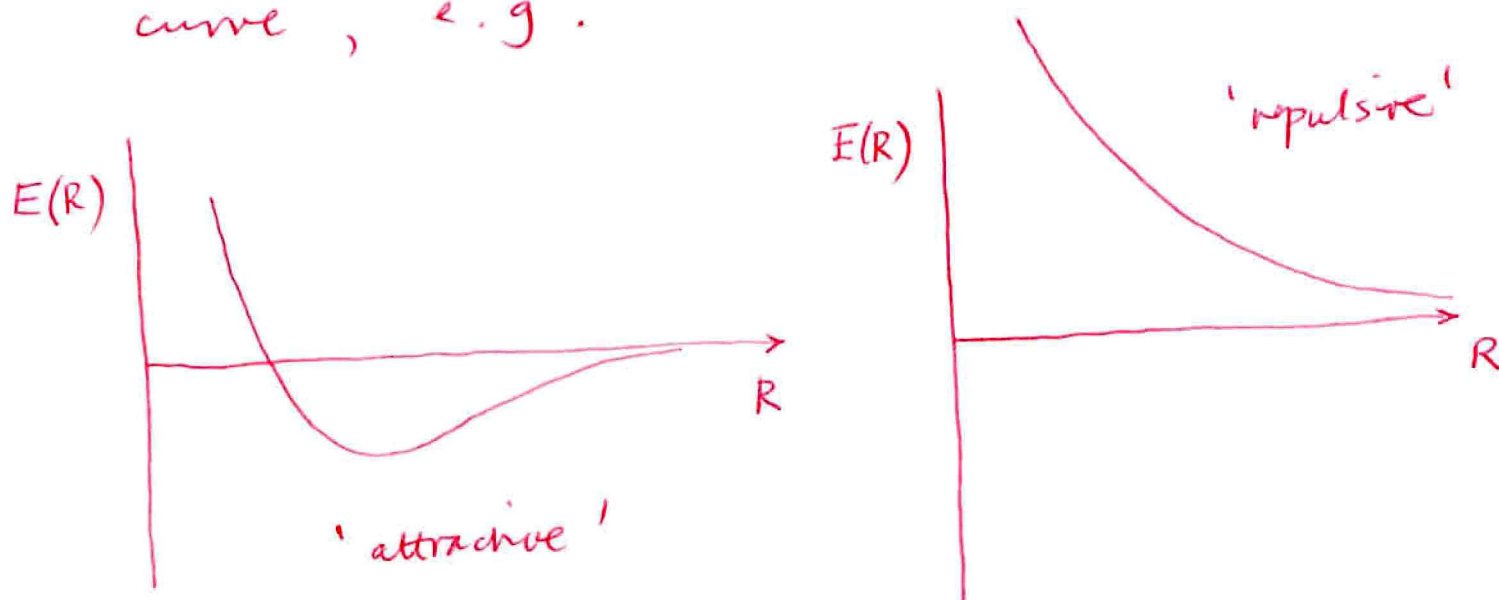
$$(H - E)\,\overline{\Psi} = \left[-\frac{\hbar^2}{2m_e} \sum_{i=1}^{2} \vec{\nabla}_i^{\,2} (x_i, y_i, z_i) \right.$$

$$+ \frac{e^2}{|\vec{r_1} - \vec{r_2}|} - \frac{e^2}{|\vec{R_1} - \vec{r_1}|} - \frac{e^2}{|\vec{R_1} - \vec{r_2}|}$$

$$- \frac{e^2}{|\vec{R_2} - \vec{r_1}|} - \frac{e^2}{|\vec{R_2} - \vec{r_2}|}$$

$$\left. - E \right] \psi(\vec{r_1}, \vec{r_2})$$

$$= 0$$

where $\vec{R_1} = \left(0, 0, -\frac{R}{2}\right)$

and $\vec{R_2} = \left(0, 0, \frac{R}{2}\right)$

The 12-dimensional problem has been reduced to 6-dimensional, for given R.

Departures from the B-O approximation can be significant under certain conditions. Indeed, some important interstellar processes occur owing to such departures. Nonetheless, the B-O approximation is a sensible starting-point when treating systems of interacting atoms. The energy of such a system, $E(R)$, calculated using the B-O approximation is often referred to as an 'adiabatic' potential energy curve, e.g.

'attractive'

'repulsive'

Only 'attractive' potential energy curves can support bound states of molecules.

Symmetry Properties

Symmetry operations and properties form the basis of much of physical science and of atomic and molecular physics, in particular; this is increasingly the case as the systems being studied become more complex.

The underlying reason for the importance of symmetry considerations, in the context of quantum mechanics, is that the eigenfunctions of symmetry operators which leave the hamiltonian invariant are also <u>eigenfunctions of the hamiltonian</u>, which are the quantities which we are seeking.

To each conserved quantity (energy, linear momentum, angular momentum, ...), there corresponds a symmetry operation (translation in time, translation in space, rotation in space, ...). Identifying the symmetry operators, their eigenfunctions and eigenvalues, is tantamount to finding solutions of the Schrödinger equation for the corresponding coordinates.

Some examples of symmetry operations :

(i)   Any plane through the internuclear axis (also called the 'symmetry axis') is a plane of symmetry. Reflection of the coordinates of all electrons in this plane leaves the hamiltonian invariant. As a second reflection restores the original configuration, we have that

$$R^2 \bar{\Psi} = \bar{\Psi}$$

or

$$R \bar{\Psi} = \pm \bar{\Psi}$$

where R is the reflection operator. Thus, the electron wavefunction is unchanged or changes its sign when a reflection of electron coordinates occurs. This symmetry is denoted '+' or '−'.

(ii)   Following the same reasoning as in (i) above, it may be seen that, in homonuclear molecules such as H_2 (more generally, in molecules where the nuclei have the same charge), the electron wave function is invariant or changes only its sign when the coordinates of the electrons are reflected in the centre of charge, i.e. the eigenvalues of this inversion operator are ± 1. This symmetry is denoted 'gerade' (g) or 'ungerade' (u).

(iii) Exchange of electrons also leaves the hamiltonian invariant, and, once again, the eigenvalues are ± 1. However, only the solution with eigenvalue -1 is allowed by the <u>Pauli Exclusion Principle</u>, which applies to fermions (particles, such as electrons and protons, which have $\frac{1}{2}$-integral spin).

[In the case of particles with integral spin, only the solution with eigenvalue $+1$ is allowed.]

Angular momenta

Orbital angular momentum : in the hydrogen <u>atom</u>, which has <u>spherical symmetry</u>, the electron can have orbital angular momentum $l = 0, 1, 2, 3, 4, \ldots$ For historical reasons, these angular momentum states are denoted $s, p, d, f, g, \ldots$ When more than one electron is involved, the total orbital angular momentum is denoted L and upper case letters ($S, P, D, \ldots$) are used.

In the hydrogen <u>molecule</u>, and more generally in linear molecules, the symmetry is <u>axial</u>.

The relevant quantum number is not L, but the projection of $\vec{L}$ on the internuclear axis, M_L.

Furthermore, the sense of rotation about the internuclear axis is irrelevant, in this context, i.e. states $\pm M_L$ have the same energy. They are distinguished by the absolute value of M_L, $|M_L|$, and states with $|M_L| = 0, 1, 2, \dots$ are denoted $\Sigma, \Pi, \Delta, \dots$ by analogy with the atomic case.

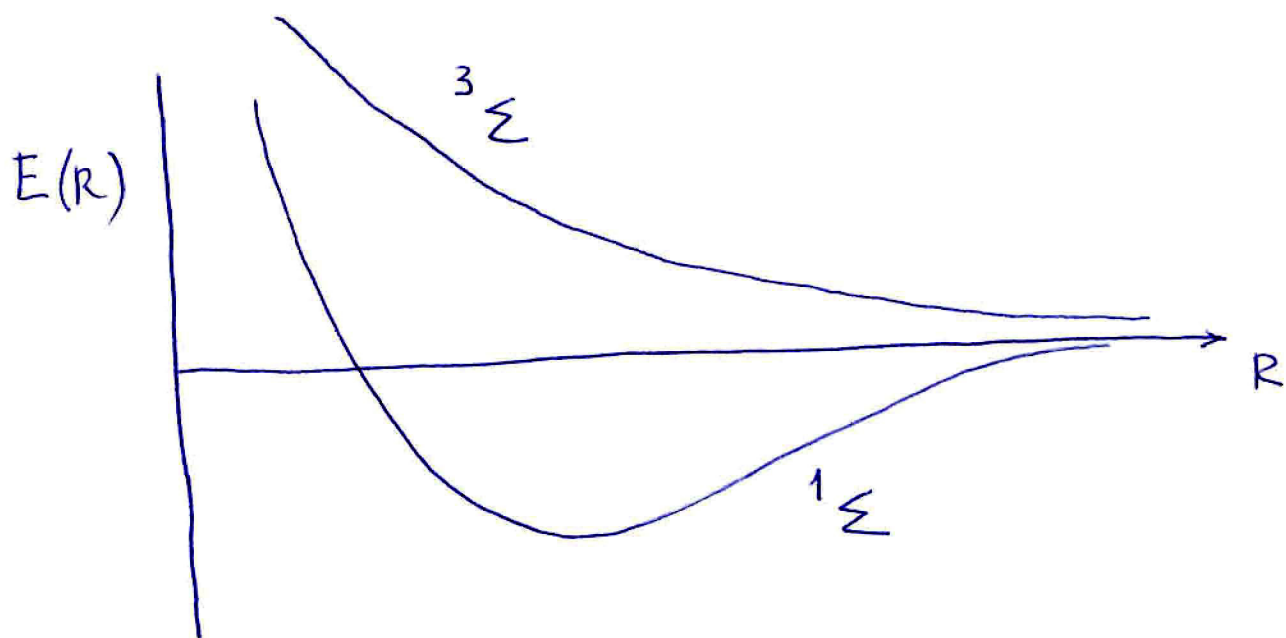Spin angular momentum : electrons are fermions ($s = \frac{1}{2}$, where s is the spin quantum number). Two electrons (He atom, H_2 molecule) form states with total spin $S = 0$ or $S = 1$, corresponding to the individual electron spins being anti-parallel or parallel. These total spin states are referred to as a singlet and a triplet, respectively =

there is only one possible value of the projection on the z-axis, $M_S = 0$, in the former case; in the latter case, there are three possible values, $M_S = 0, \pm 1$. [See also the discussion of nuclear spin below.]

The example of H_2

When two H atoms approach each other, each in its electronic ground state (the usual case in the ISM), the value of $|M_L|$ is zero, as both the electrons have zero orbital angular momentum; $|M_L| = 0$ is denoted Σ, as was mentioned above. The total electron spin $S = 0$ or $S = 1$ (singlet or triplet), and the corresponding multiplicity is written as a preceding superscript (to Σ). Thus, two H atoms in their ground states can form H_2 $^1\Sigma$ or $^3\Sigma$. The corresponding potential energy curves have the form:
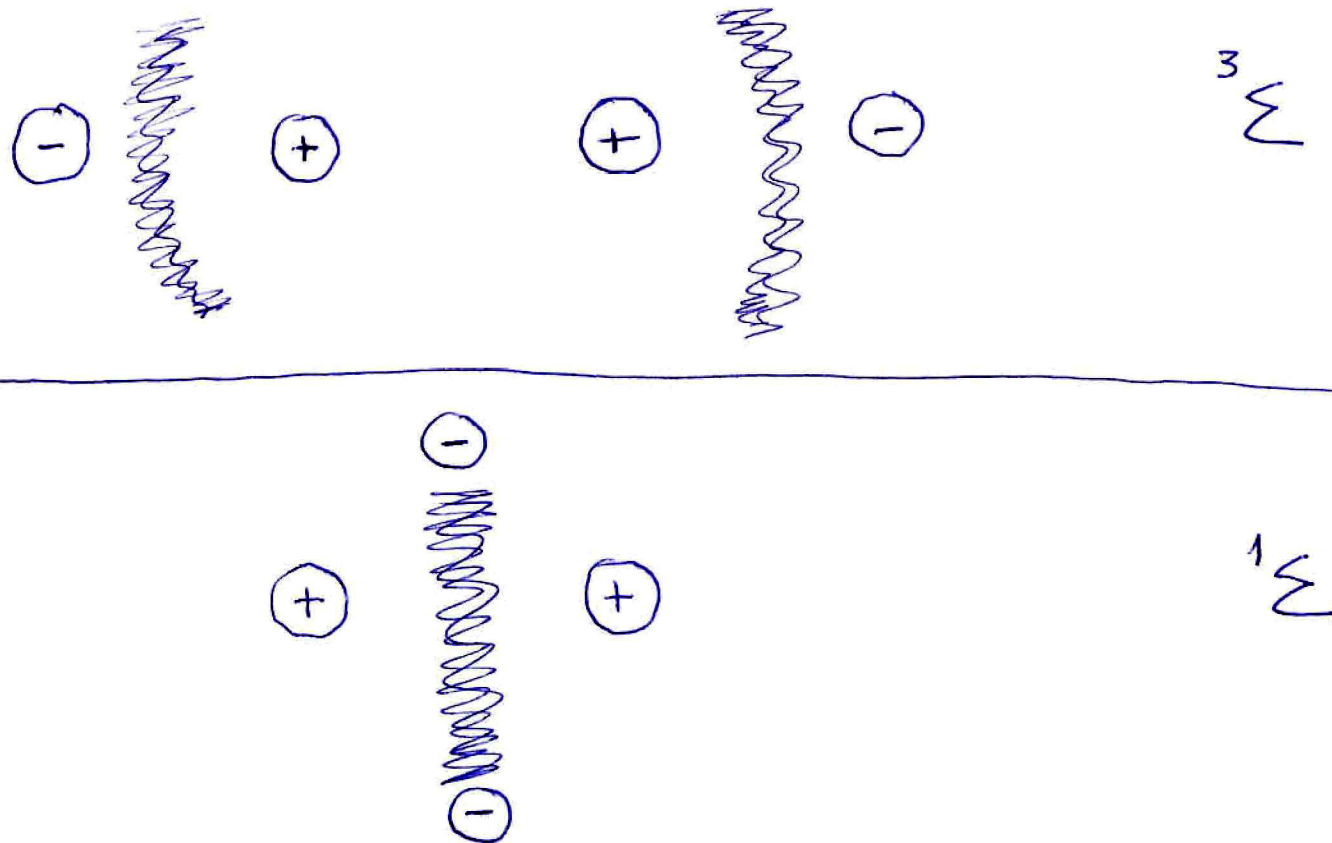

It may be seen that the $^3\Sigma$ state is repulsive: a bound H_2 molecule cannot form in this electronic state.

The $^1\Sigma$ state is attractive at long range and repulsive at short range and hence has a potential minimum (potential well); the $^1\Sigma$ state is the ground state of the H_2 molecule. Introducing the other quantum numbers, considered above, the full spectroscopic designation of the H_2 ground electronic state is $X\,^1\Sigma_g^+$, where 'X' signifies that it is the ground state (there can be other electronic states of $^1\Sigma_g^+$ symmetry).

The reason that the $^3\Sigma$ state is repulsive and the $^1\Sigma$ state is attractive relates to the Pauli Exclusion Principle. In the limit of $R \to 0$ (the 'united atom' limit), an atom of He is formed in its ground state. As is well known, He can exist only in its singlet state when both electrons have $n = 1$ and $l = 0$ (the ground state is denoted $1s^2\,^1S$; the state $1s^2\,^3S$ is forbidden by the Exclusion Principle). Thus, when two $H(1s)$ atoms approach each other, the Exclusion Principle causes the triplet state to be repulsive (a molecule cannot form in this state), whereas the singlet state has a well.

The charge distributions look like this:

$$^3\Sigma$$

$$^1\Sigma$$

In the $^3\Sigma$ state, the electrons are kept apart by the Exclusion Principle, and the Coulomb repulsion between the nuclei prevents the formation of a stable H_2 molecule.

In the $^1\Sigma$ state, the electrons have a high probability of being found between the nuclei, thereby partially screening the nuclear charge and enabling a bound molecule to form.

Given the charge distribution, it is clear that H_2 does not possess a permanent dipole moment in its ground electronic state; it does possess a permanent quadrupole moment.
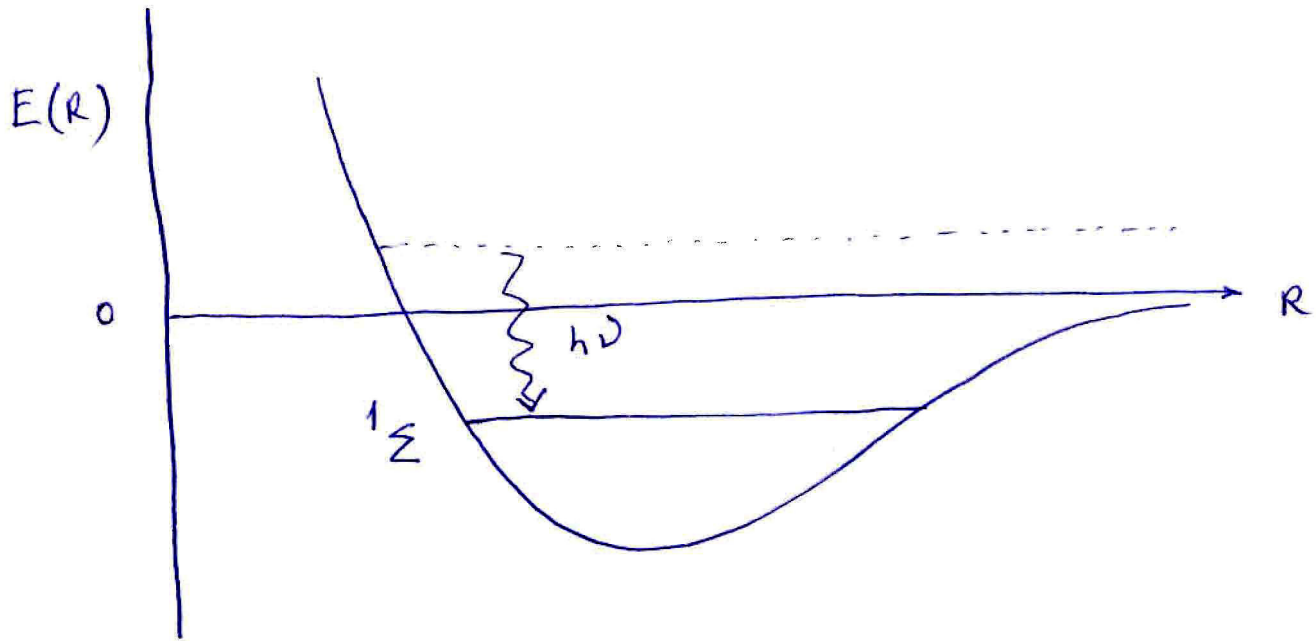
A parenthetic comment on the formation of H_2 in the ISM.

Why does H_2 not form at a significant rate in the gas phase in the ISM ?

(i) In the gas phase, the frequency of 3-body collisions, which can lead to the formation of H_2, is negligible (for particle densities $n_H \lesssim 10^8 cm^{-3}$, which excludes even 'dense' molecular clouds). Thus, the process must be 2-body, and the energy required to stabilize the molecule, when it forms from two atoms, is carried away by a photon. Radiative processes are slow.

(ii) If the two (ground state) atoms approach along the $^3\Sigma$ curve, formation of a bound H_2 molecule involves a radiative transition to the $^1\Sigma$ state. However, such transitions are forbidden to electric dipole radiation, as they involve a change in the total electron spin (from $S=1$ to $S=0$). [Total spin-changing transitions can occur, owing to magnetic interactions (i.e. relativistic effects), but their associated probabilities are small.]

(iii) If the atoms approach along the $^1\Sigma$ curve, the molecule can stabilize by a radiative transition from a continuum to a bound rovibrational state :
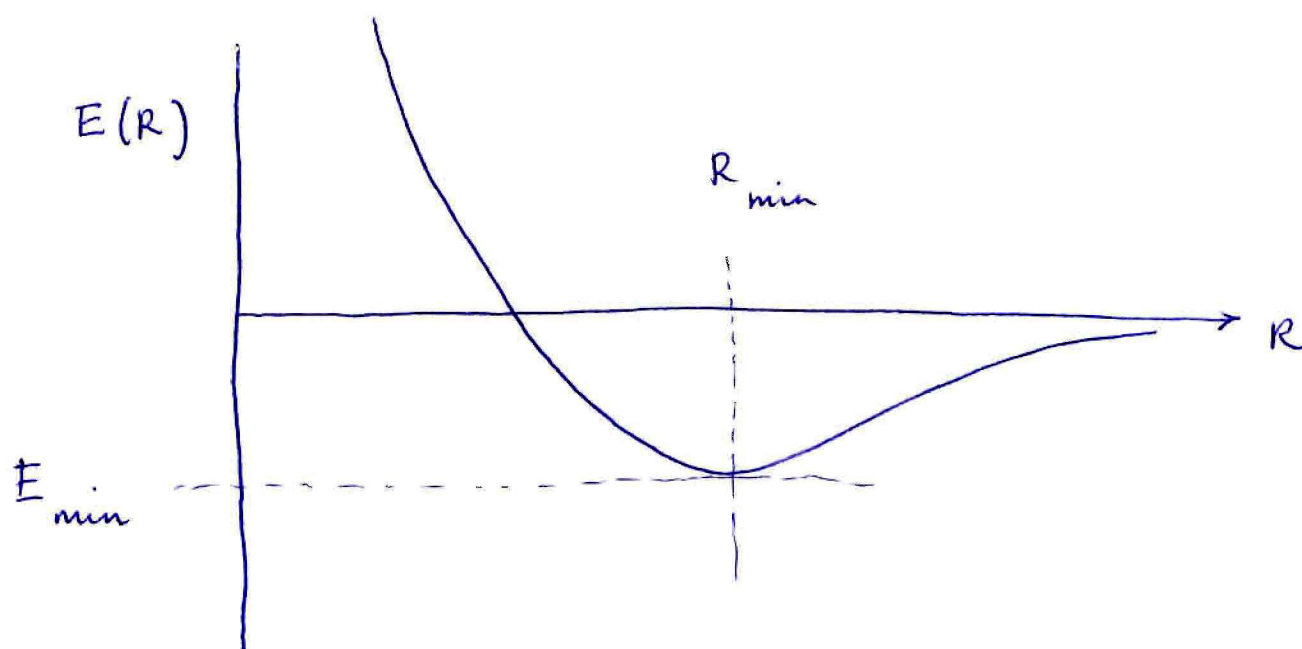

However, as already noted, the H_2 molecule has no permanent electric dipole moment in its electronic ground state; its first non-vanishing permanent electric multipole moment is quadrupole. Thus, the radiative transition is electric quadrupole, and it has a low probability.

Consequently, H_2 formation is believed to occur on grains. The energy required to stabilize the molecule is transferred to the grain (in fact, to the phonon spectrum of the grain); coupling to the radiation field is not involved.

Rovibrational states of H_2

We consider the $X\ ^1\Sigma_g^+$ electronic ground state :

$$E_{min} \approx -40\ 000\ cm^{-1}\ (\approx 5\,eV)\ at\ R_{min} \approx 0.75\,\mathring{A}$$

$$[\ 1\,\mathring{A} \equiv 10^{-10}\,m\ ]$$

Although the nuclei move much more slowly than the electrons, nonetheless they perform relative motion in the R coordinate and 'end-over-end' rotational motion in the (Θ, Φ) coordinates. [R is the magnitude of the internuclear separation and (Θ, Φ) define the orientation of the internuclear axis, with respect to a <u>space-fixed</u> (or 'laboratory') reference frame.

Let us denote the interaction energy $E(R)$ by $V(R)$, in order to use E to represent the total nuclear rovibrational energy. In effect, the nuclei move in a potential $V(R)$ which has been determined using the B–O approximation. We have to solve the corresponding Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu} \vec{\nabla}_R^2 + V(R) \right] \psi(\vec{R}) = E \psi(\vec{R})$$

where $\vec{R} \equiv (R, \Theta, \Phi)$ and the reduced mass, μ, is the product of the masses of the nuclei, divided by their sum, i.e.,

$$\mu = \frac{m_p^2}{2m_p} = \frac{m_p}{2}.$$

When writing the Schrödinger equation in this form, we make use of the fact that the relative motion of the nuclei may be considered equivalent to the motion of a particle of reduced mass μ relative to a fixed centre, distant by R, together with the (constant velocity) motion of the centre of mass (CM) of the nuclei. This latter motion may be removed by simply imposing a constant velocity shift $-\vec{v}_{CM}$ on the system.

In cartesian coordinates, $\vec{R} = (X, Y, Z)$ and

$$\vec{\nabla}_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$$

In spherical polar coordinates, $\vec{R} = (R, \Theta, \Phi)$ and

$$\vec{\nabla}_R^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin \Theta} \frac{\partial}{\partial \Theta} \left(\sin \Theta \frac{\partial}{\partial \Theta} \right)$$

$$+ \frac{1}{R^2 \sin^2 \Theta} \frac{\partial^2}{\partial \Phi^2}$$

Spherical polar coordinates are better adapted to the symmetry of this problem.

A solution may be found by separation of variables.

As shown in standard texts on quantum mechanics, the solution takes the form

$$\Psi (R, \Theta, \Phi) = F(R) \, Y(\Theta, \Phi)$$

where $Y(\Theta, \Phi)$ is a spherical harmonic.

Physically acceptable solutions are such that

$$Y(\Theta, \Phi) = Y_{JM}(\Theta, \Phi)$$

where J and M are integers and

$$-J \leq M \leq J$$

J may be identified with the rotational angular momentum quantum number and M with the projection of the rotational angular momentum on the Z-axis. Y_{JM} is the rotational eigenfunction.

The equation for the radial function, $F(R)$, takes the form:

$$-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{d}{dR} \left[R^2 \frac{d}{dR} F(R) \right] + \frac{J(J+1)\hbar^2}{2\mu R^2} F(R)$$

$$+ V(R) F(R) = E F(R)$$

The first term on the left-hand side corresponds to the radial kinetic energy, the second to the rotational kinetic energy, as may be seen as follows.

Classically,
$$\vec{J} = I\vec{\omega}$$

where I is the moment of inertia and $\vec{\omega}$ is the angular velocity. The rotational kinetic energy is

$$\frac{1}{2} I \vec{\omega}^2 = \frac{1}{2} I \frac{\vec{J}^2}{I^2} = \frac{1}{2I} \vec{J}^2$$

Now, $I = \mu R^2$ and hence $\frac{1}{2} I \vec{\omega}^2 = \frac{1}{2\mu R^2} \vec{J}^2$

Introducing the quantum mechanical equivalent of $\vec{J}^2$, $J(J+1)\hbar^2$, we obtain $\dfrac{J(J+1)\hbar^2}{2\mu R^2}$

as the equivalent of the classical expression for the rotational kinetic energy, $\dfrac{1}{2}I\vec{\omega}^2$.

Substituting $F(R) \equiv \dfrac{\chi(R)}{R}$, the radial equation becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}\chi(R) + \frac{J(J+1)\hbar^2}{2\mu R^2}\chi(R) + V(R)\chi(R)$$

$$= E\,\chi(R)$$

The rotational kinetic energy, $\dfrac{J(J+1)\hbar^2}{2\mu R^2}$, may also be termed the centrifugal potential

One may then define an effective potential,

$$V_{eff}(R) = V(R) + \frac{J(J+1)\hbar^2}{2\mu R^2}$$

comprising the interaction potential and the centrifugal potential (which is repulsive).

(21)

The radial functions, $\chi(R)$, have to be derived by solving numerically the radial equation. As is usually the case in Physics, _approximations_ can provide insight:

— $J = 0$

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V(R) \right] \chi(R) = E\chi(R)$$

Near the bottom of the potential well, the interaction potential, $V(R)$, can often be approximated accurately by a harmonic potential,

$$V(R) \approx \frac{1}{2} K (R - R_{min})^2$$

where K is a constant, dependent on the molecule being studied. The solutions to this equation are the _harmonic oscillator eigenfunctions_, which have the corresponding eigenenergies

$$E_v = \left(v + \frac{1}{2}\right) \hbar \sqrt{\frac{K}{\mu}}$$

in which the vibrational quantum number, $v = 0, 1, 2, \dots$

Note that, even when $v = 0$, the vibrational energy is finite: $E_0 = \frac{1}{2} \hbar \sqrt{\frac{K}{\mu}}$. Owing to this _zero-point vibrational energy_, the dissociation energy of a molecule in its vibrational ground state is smaller than the depth of the potential well by E_0.

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— $J > 0$. If one adopts the expectation value of R^2 in the appropriate vibrational state, v,

$$\langle R^2 \rangle_v \equiv \langle \chi_v | R^2 | \chi_v \rangle = \int \chi_v^* R^2 \chi_v \, dR,$$

then the rotational energy may be written as

$$B_v \, J(J+1)$$

where

$$B_v = \frac{\hbar^2}{2\mu \langle R^2 \rangle_v}$$

In the case of H_2, $\mu = \dfrac{m_p}{2}$, and, taking $\langle R^2 \rangle_0 = 0.75 \text{ Å}$ in the $v=0$ vibrational ground state, we obtain

$$B_0 = 59.5 \text{ cm}^{-1}$$

which is close to the spectroscopic (experimentally measured) value of 59.3 cm^{-1}.

The spectroscopic value of the vibrational level spacing in the ground electronic state of H_2 is

$$\hbar \sqrt{\frac{K}{\mu}} = 4395 \text{ cm}^{-1}$$

and hence $K \approx 10^3 \text{ N m}^{-1}$.

In the harmonic oscillator approximation, the restoring force on displacement from the position of equilibrium is

$$F_R = -K(R - R_{min})$$

Taking $|R - R_{min}| = 0.01 \text{ Å} = 10^{-12} \text{ m}$, we obtain $|F_R| \simeq 10^{-9} \text{ N}$. The weight of a hydrogen molecule is $2m_p g \simeq 3 \times 10^{-26} \text{ N}$. Thus, a small displacement from equilibrium, by 0.01 Å, gives rise to a force which is sufficient to support approximately 10^{16} times the molecule's own weight. Molecular bonds are very strong.

Symmetry properties of the nuclear wavefunctions of H_2

The Pauli Exclusion Principle applies to all particles with $\frac{1}{2}$-integral spin angular momentum and hence to the protons of H_2. The relative nuclear coordinates are $\vec{R} \equiv (R, \Theta, \Phi)$, and we have seen that the nuclear wave function is

$$\psi(\vec{R}) = \frac{x(R)}{R} Y_{JM}(\Theta, \Phi)$$

Exchange of the (identical) nuclei is equivalent to changing $\vec{R}$ to $-\vec{R}$. A second exchange restores the original configuration. Thus, the proton-exchange operator has eigenvalues of ± 1; and the Exclusion Principle states that only those states with the eigenvalue -1 occur in Nature.

The operation $\vec{R} \rightarrow -\vec{R}$ corresponds to

$$(R, \Theta, \Phi) \longrightarrow (R, \pi - \Theta, \pi + \Phi)$$

From the properties of the spherical harmonics, it may be shown that

$$Y_{JM}(\pi - \Theta, \pi + \Phi) = (-1)^J Y_{JM}(\Theta, \Phi)$$

Hence,

$$\psi(-\vec{R}) = (-1)^J \psi(\vec{R})$$

The possible states of total nuclear spin, I, are:

		M_I
$I = 1$ ('triplet')	$\alpha_1 \alpha_2$	1
	$2^{-1/2}(\alpha_1 \beta_2 + \alpha_2 \beta_1)$	0
	$\beta_1 \beta_2$	-1
$I = 0$ ('singlet')	$2^{-1/2}(\alpha_1 \beta_2 - \alpha_2 \beta_1)$	0

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α and β are the individual 'spin-up' and 'spin-down' functions.

Under proton exchange, $1 \longleftrightarrow 2$, the triplet functions are symmetric, whereas the singlet function is asymmetric. As the total nuclear wave function is a <u>product</u> of the spatial component, $\psi(\vec{R})$, and the spin component, it may be seen that

- triplet states must associate with odd J
- singlet states must associate with even J

in order to satisfy the Exclusion Principle.

- The triplet nuclear spin states of H_2 are <u>ortho</u> states
- The singlet nuclear spin states of H_2 are <u>para</u> states
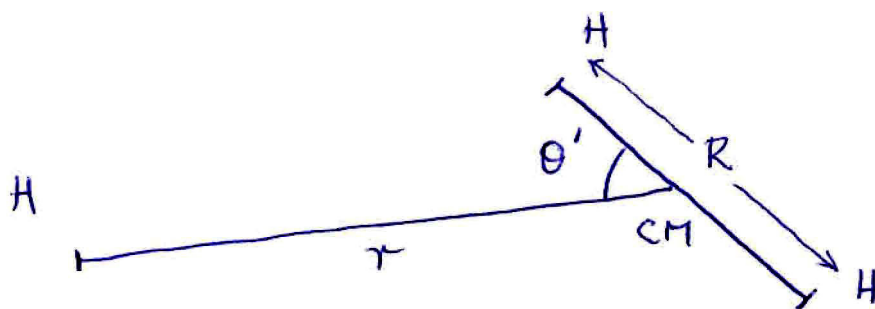
Transitions from ortho to para or para to ortho involve a <u>change of nuclear spin</u>. In practice, such transitions can occur only in proton-exchange reactions with species such as H^+ and H_3^+ (in cold molecular gas) or with H (in shocks: the reaction with H has a barrier of approximately 5000 K).

Atom - molecule collisions

We shall consider the example of $H - H_2$ collisions, although this system is not the simplest to treat, in general. The incident H atom may exchange with an atom bound in the molecule. As noted already, this reaction has a barrier of approximately 5000 K. For collision energies $E \ll 5000 K$, the reactive scattering channels may be neglected = only rovibrationally inelastic scattering is significant.

Let us continue to denote by $\vec{R} = (R, \Theta, \Phi)$ the intramolecular vector. Furthermore, let $\vec{r} = (r, \theta, \varphi)$ denote the vector joining the incident atom to the centre of mass of the molecule. These coordinates are relative to a <u>space-fixed</u> (laboratory) reference frame.

We may consider the incident atom to move relative to a fixed point (the centre of mass of the molecule) with reduced mass

$$\mu = \frac{m_A \, m_{BC}}{m_A + m_{BC}},$$

where m_{BC} is the mass of the molecule (considered to be located at the CM). In the example of $H - H_2$ scattering,

$$\mu = \frac{m_p \, 2 m_p}{3 m_p} = \frac{2}{3} m_p.$$

In order to solve the collision problem, the interaction potential has to be calculated. Using the B–O approximation, this interaction may be derived, for fixed relative nuclear coordinates, by means of an energy minimization procedure. The potential

$$V = V(R, r, \theta'),$$

as may be appreciated by referring to the above Figure. In other words, the atom – molecule interaction is expressed most naturally in a coordinate system in which the intramolecular axis is taken to be the z-axis. This body-fixed coordinate system rotates relative to the space-fixed system in the course of the collision. Both centrifugal and Coriolis forces arise from this rotation.
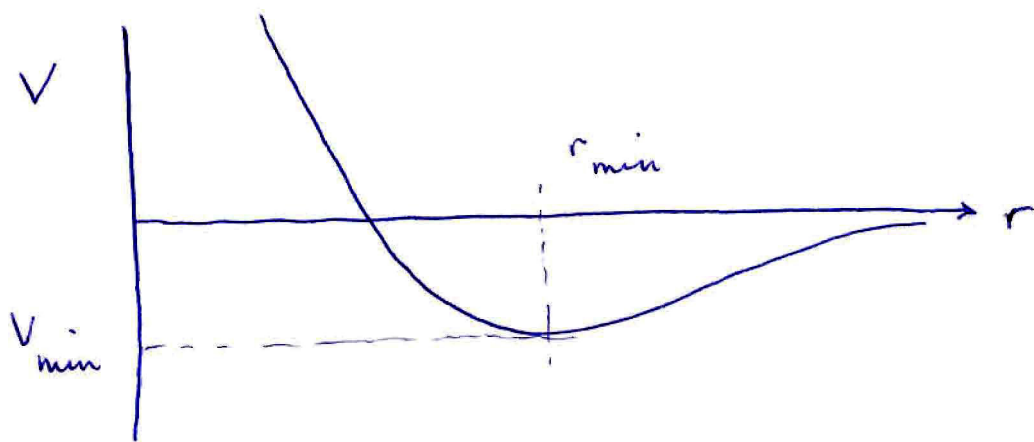
At infinite separation of the atom from the molecule, the interaction energy, as calculated using the B-O approximation, is the sum of the binding energies of the particles in the atom and the particles in the molecule. The sum of these energies is of the order of 1 hartree (the hartree is the atomic unit of energy $\approx$ 200 000 cm^{-1} $\approx$ 300 000 K).

At long range, the atom-molecule potential is weakly attractive, owing to the van der Waals interaction.

At short range, the potential is strongly repulsive, owing to the Coulomb interactions between the electrons and between the nuclei.

At intermediate range, there is a potential minimum:

Typically, $r_{min} \approx 7\, a_0$ and $V_{min} \approx 10$ cm^{-1}.

V_{min} is computed as the _difference_ between the B-O interaction energy at r_{min} and the B-O energy at very large r $(r \to \infty)$, i.e. V_{min} is the _very small difference_ $(\approx 10 \text{ cm}^{-1})$ between two large numbers $(\approx 200\,000 \text{ cm}^{-1})$. This is the basic difficulty faced by those who calculate atom – molecule interaction potentials.

Note that $V(R, r, \Theta')$ has to be computed on grids of values of R, r, and Θ'. The output of the potential computation is

$$V(R_i, r_j, \Theta'_k), \quad \begin{aligned} i &= 1, 2, \ldots, l \\ j &= 1, 2, \ldots, m \\ k &= 1, 2, \ldots, n \end{aligned}$$

or a total of $l \times m \times n$ energies. In the case of atom – homonuclear molecule interactions, such as $H - H_2$, some saving of effort may be made as

$$V(R, r, \Theta') \equiv V(R, r, \pi - \Theta')$$

How can these interaction energies be best used?

Fitting the potential

Rather than attempting to use the raw data,
$V(R_i, r_j, \theta'_k)$, it is much better to fit
the potential to appropriate functions of the angular
coordinate, θ'. The Legendre polynomials,

$P_\lambda(\cos\theta')$ $[\lambda = 0, 1, 2, \ldots]$, form a
complete set of functions of θ'. In other words,

$$V(R, r, \theta') = \sum_{\lambda=0}^{\infty} v_\lambda(R, r) P_\lambda(\cos\theta')$$

is an exact representation of the potential, V;
v_λ are the expansion coefficients and

$$P_0 = 1, \quad P_1 = \cos\theta', \quad P_2 = \frac{3\cos^2\theta' - 1}{2}$$

In practice, V is known on a finite angular
grid, θ'_k $[k \leq n]$, and hence only a finite
number of terms, λ, can be determined. As λ
increases, the expansion should converge, in the sense
that $|v_\lambda|$ should decrease as λ increases beyond
a certain value.

We may use the fact that

$$\int_{-1}^{1} P_\lambda(\cos\theta') \, P_{\lambda'}(\cos\theta') \, d\cos\theta' = \delta_{\lambda\lambda'} \frac{2}{2\lambda+1}$$

to show that

$$v_\lambda(R,r) = \frac{2\lambda+1}{2} \int_{-1}^{1} P_\lambda(\cos\theta') \, V(R,r,\theta') \, d\cos\theta'$$

Knowing V, v_λ may be calculated for a finite number of values of λ.

Note that the expansion

$$V(R,r,\theta') = \sum_\lambda v_\lambda(R,r) \, P_\lambda(\cos\theta')$$

is expressed in the body-fixed frame, whereas the collision occurs in the space-fixed frame. In order to transform the potential expansion to the space-fixed frame, we make use of the spherical harmonic addition theorem:

$$P_\lambda(\cos\theta') = \frac{4\pi}{2\lambda+1} \sum_{\nu=-\lambda}^{\lambda} Y_{\lambda\nu}(\hat{r}) \, Y_{\lambda\nu}^{*}(\hat{R})$$

where $\hat{r} = (\theta,\varphi)$ and $\hat{R} = (\Theta, \Phi)$ are angular coordinates in the space-fixed frame.

The Schrödinger equation for $H - H_2$ scattering is similar in form to that obtained above, when considering the isolated molecule. The Schrödinger equation may be written

$$\left[h - \frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V \right] \overline{\Psi} = E\overline{\Psi}$$

where $\vec{l}$ is the orbital angular momentum of the atom, of reduced mass μ, relative to the centre of mass of the molecule, and $\overline{\Psi} = \overline{\Psi}(\vec{R}, \vec{r})$; h is the internal Hamiltonian of the isolated molecule, considered above.

By making use of the appropriate angular momentum algebra, the Schrödinger equation may be expressed as a set of coupled, second order, differential equations in the radial coordinate, r, involving the quantum numbers:

v	vibration
J	internal rotation
l	relative orbital angular momentum
J_{tot}	total angular momentum
	$(\vec{J}_{tot} = \vec{J} + \vec{l})$
$p = (-1)^{J+l}$	inversion parity

Both J_{tot} and p are 'good' quantum numbers, i.e. they correspond to <u>conserved</u> quantities.

Sets of coupled equations have to be solved for $J_{tot} = 0, 1, 2, \ldots$ and $p = \pm 1$. The results eventually converge, in the sense that the contributions to the cross sections from 'large' values of J_{tot} become negligible (what is meant by 'large' depends on the collision energy, E).

Cross sections and rate coefficients

Cross sections, σ, have units of area. The square of the wave number, $k^2 = 2\mu E / \hbar^2$, has dimensions of 1/area. It may be shown that, owing to microscopic time-reversal symmetry, the dimensionless quantity $\sigma \omega k^2$, where ω is a statistical weight, is invariant. Specifically,

$$\sigma(vJ \leftarrow v'J')(2J'+1) k^2_{v'J'} =$$

$$\sigma(v'J' \leftarrow vJ)(2J+1) k^2_{vJ}$$

where $k^2_{vJ} = \dfrac{2\mu}{\hbar^2}(E - E_{vJ})$ and E_{vJ} is the excitation energy of the level (v, J).

It is generally assumed that *elastic* collisions between gas particles (elastic cross sections are larger than inelastic cross sections) establish a <u>Maxwell distribution</u> of velocities,

$$f(v, T) = 4\pi \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(- \frac{\mu v^2}{2 k_B T} \right)$$

where v is the relative collision speed, k_B is Boltzmann's constant, and T is the kinetic temperature.

One may define the <u>rate coefficient</u> as

$$\langle \sigma v \rangle = \int_0^\infty v\, \sigma(v)\, f(v, T)\, dv$$

$$= \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2} \int_0^\infty x\, \sigma(x)\, e^{-x}\, dx$$
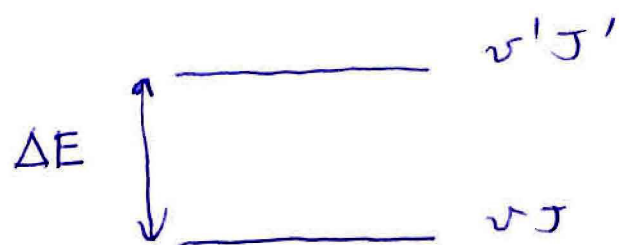
where $\left(8 k_B T / \pi \mu \right)^{1/2}$ is the mean thermal speed of the particle with reduced mass μ and $x \equiv \mu v^2 / (2 k_B T) = \frac{E}{k_B T}$.

Noting that $x = \dfrac{E}{k_B T} = \dfrac{\hbar^2 k^2}{2\mu k_B T}$,

the time-reversal symmetry relation may be written

$$\sigma \left(vJ \leftarrow v'J' \right) (2J'+1)\, x_{v'J'} = \sigma \left(v'J' \leftarrow vJ \right) (2J+1)\, x_{vJ}$$

Let vJ be the lower and $v'J'$ be the upper level:

$$v'J'$$

$$\Delta E$$

$$vJ$$

Then, $\qquad x_{v'J'} + \dfrac{\Delta E}{k_B T} = x_{vJ}$.

Multiplying both sides of the time-reversal symmetry relation by $e^{-x_{vJ}}$ and then integrating with respect to x, we obtain

$$(2J'+1)\, e^{-\Delta E/k_B T} \int_0^\infty x_{v'J'}\, \sigma(vJ \leftarrow v'J')\, e^{-x_{v'J'}}\, dx_{v'J'}$$

$$= (2J+1) \int_0^\infty x_{vJ}\, \sigma(v'J' \leftarrow vJ)\, e^{-x_{vJ}}\, dx_{vJ}$$

or, alternatively,

$$(2J'+1)\, e^{-\Delta E/k_B T} \langle \sigma v \rangle_{vJ \leftarrow v'J'} = (2J+1) \langle \sigma v \rangle_{v'J' \leftarrow vJ}$$

This relation is the principle of __detailed balance__,

relating the rate coefficients $\langle \sigma v \rangle$ for excitation and de-excitation. Once the rate coefficient for de-excitation (say) has been determined, that for excitation is given by detailed balance.

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Example of H − H₂

We have seen that the interaction potential may be expressed as

$$V(R, r, \theta') = \sum_\lambda v_\lambda(R, r) P_\lambda(\cos \theta')$$
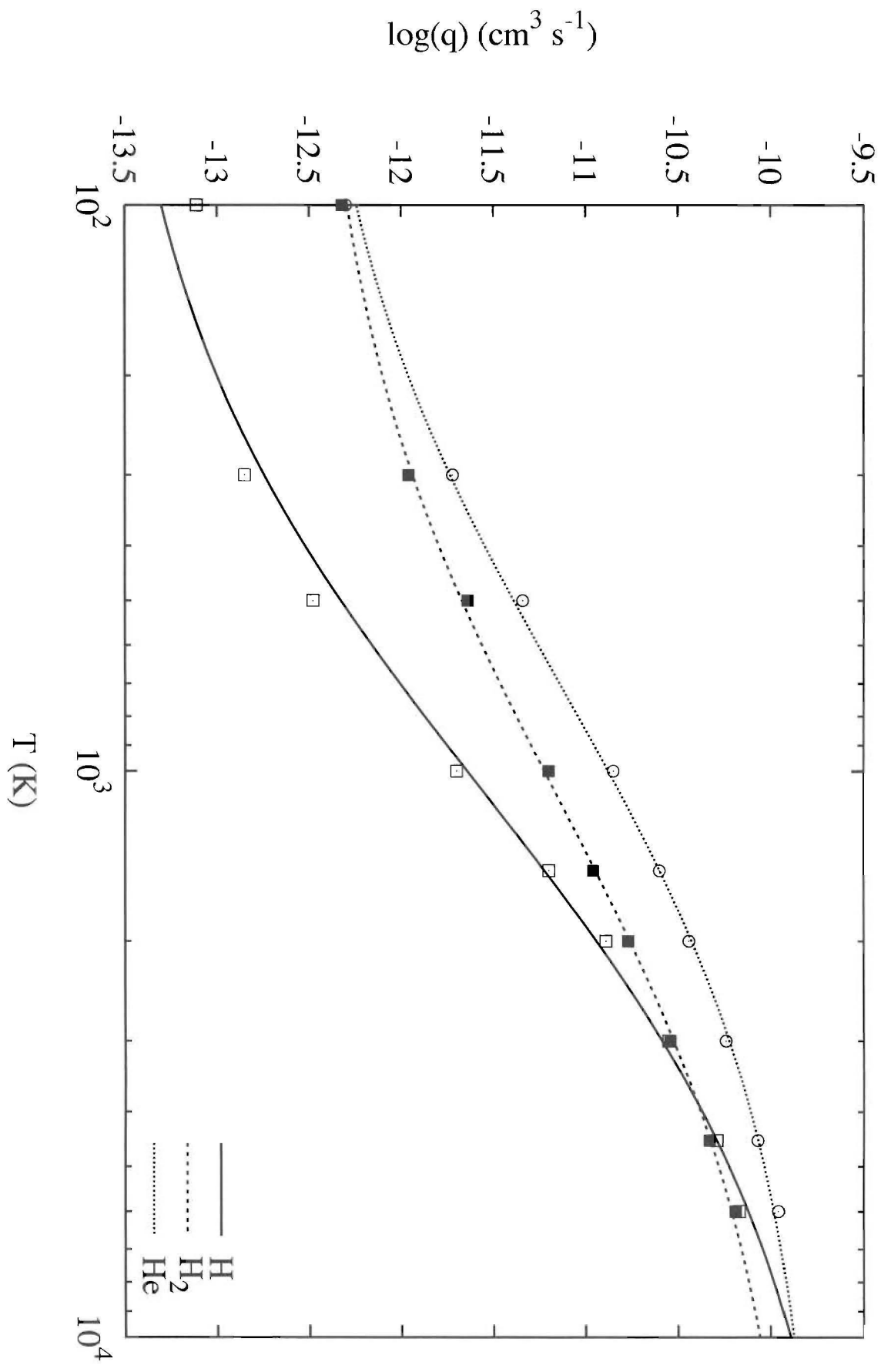
and that

$$V(R, r, \theta') = V(R, r, \pi - \theta')$$

Now, $P_\lambda(\cos \theta')$ contains only even powers of $\cos \theta'$ when λ is even, and odd powers when λ is odd.

Furthermore, $\cos(\pi - \theta') = -\cos \theta'$

Therefore, the potential expansion contains only terms of even λ. This property relates to the even J / odd J dichotomy in H_2. When λ is even, the collisional selection rules allow J to change by even increments only. Thus, if J is initially even, it remains even, if odd, it remains odd.

On the other hand, reactive collisions of H with H_2 (H atom exchange) can change even J to odd and odd J to even.
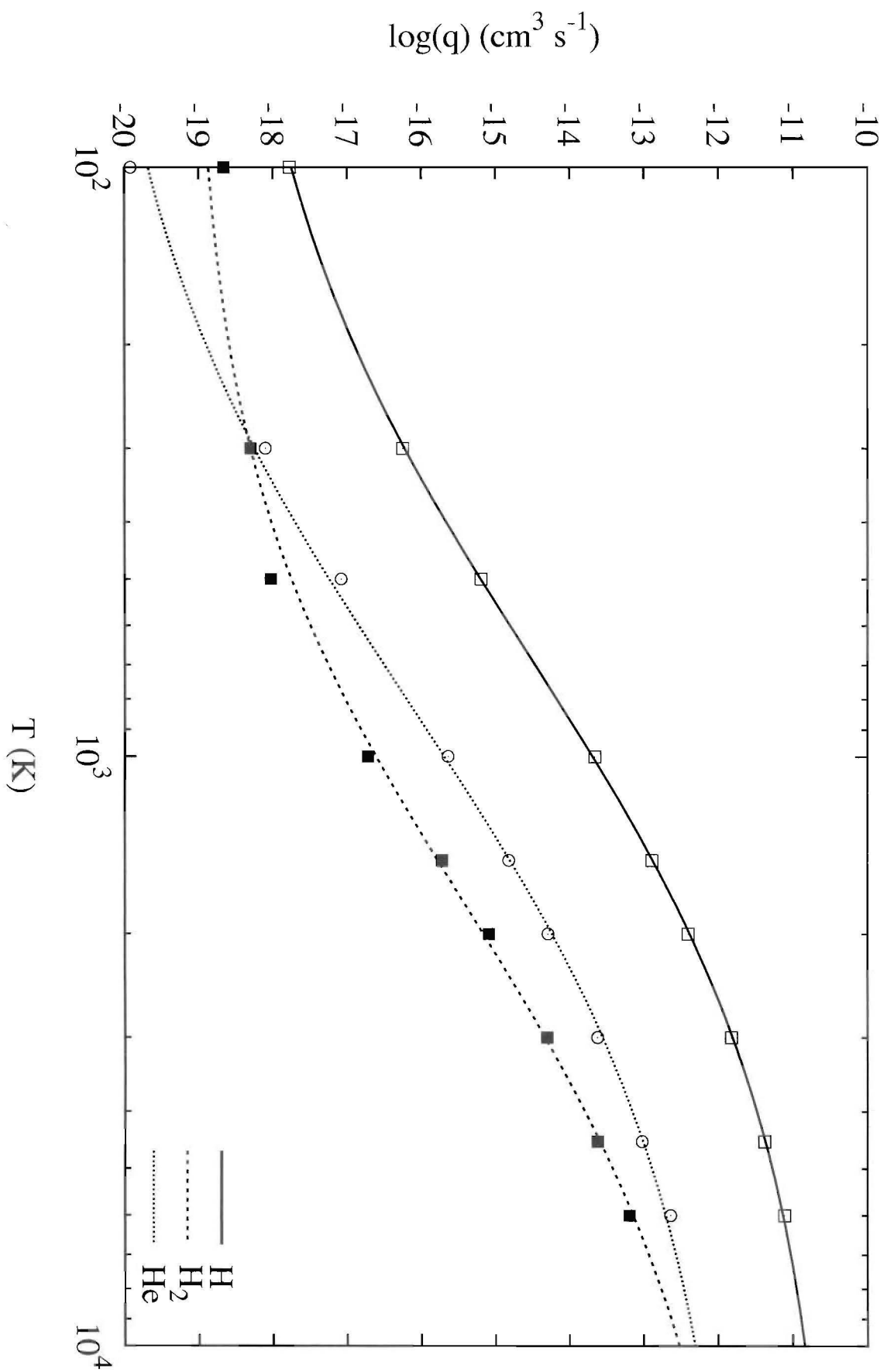
H_2 O-O S(1)

H₂ 1-0 S(1)

Allers et al. (2005)

Table 5. Model Parameters

P/k	$8 \times 10^{7} \mathrm{cm}^{-3} \mathrm{K}$
χ	3×10^{4}
$\cos(\theta)$	0.1
ζ_{CR}	$1 \times 10^{-15} \mathrm{s}^{-1}$
C/H	1.40×10^{-4}
O/H	3.56×10^{-4}
Si/H	1.74×10^{-6}
Fe/H	2.00×10^{-7}

Table 6. Comparison of $T = 1000$ K H-H_2 vibrational deexcitation rates

Reference	$k_{\mathrm{vdexc.}}(1,3)$[a]	$k_{\mathrm{vdexc.}}(2,3)$[a]
	$(\mathrm{cm}^3\,\mathrm{s}^{-1})$	
Sternberg & Dalgarno (1989)	5.5×10^{-10}	7.5×10^{-10}
Mandy & Martin (1993)	6.3×10^{-12}	3.6×10^{-11}
Le Bourlot et al. (1999)	3.5×10^{-13}	5.1×10^{-13}
present work (see text)	5.4×10^{-11}	7.9×10^{-11}

[a]For $k_{\mathrm{vdexc.}}(v, J)$ we sum over collisional transitions to all levels (v', J') with $v' < v$