# SPECTROSCOPICALLY ACCURATE CALCULATED PROPERTIES OF $H_2$

by

JASON BARKER PERRY

(Under the Direction of Phillip C. Stancil)

## ABSTRACT

Diatomic hydrogen, $H_2$, is the most abundant molecule in the universe and is therefore important in a variety of astrophysical studies. The possible cosmological time variation of physical constants, such as proton-electron mass ratio, is one example which can be probed with spectroscopic properties of $H_2$, like the rovibrational binding energies. The Born-Oppenheimer approximation can be used in the calculation of the rovibrational binding energies, which are the solutions to the Schrödinger equation. However, to achieve the most accurate calculations, the approximation must be corrected for the effects that are not considered. With the corrections, the resulting calculations are close to the experimental results. The rovibrational energies and wave functions are used to calculate the probabilities of transitions between the rovibrational levels that are due to the quadrupole moment of $H_2$. The transition probabilities and the energies are used to calculate the cooling function in the limit of large density.

INDEX WORDS: Diatomic hydrogen, Born-Oppenheimer approximation, Rovibrational levels, Quadrupole transitions, Local thermodynamic equilibrium cooling function, radiative cooling

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# DEDICATION

I dedicate this thesis to my loving family, particularly my grandmother Jocelyn Gooding who left this world long ago but will never be forgotten. I also dedicate this thesis to the African-American scientists who blazed the trail for me and my contemporaries.

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I thank all the people who helped me not only with this thesis, but throughout my graduate school experience thus far: Phillip Stancil, my major professor, members of my committee, Benhui Yang, Chih-Yuan Lin and the rest of the physics department, students and faculty. I also thank the members of my student organization, Graduate and Professional Scholars (GAPS) for their support. I thank my family for their love and encouragement. Most of all, I thank and give praise to the Almighty God for so many blessings, including the privilege of exploring the universe as a career as well as a lifestyle.

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# Chapter 1

# BOUND STATES OF $H_2$

## 1.1 Introduction

Diatomic hydrogen, $H_2$, is an important molecule for study in molecular physics and astrophysics. It is the most plentiful species in the known universe, and what is known about such properties as fine structure, Stark and Zeeman effects, electronic transitions, and nuclear spin have come from studying $H_2$ or hydrogen in general. The possible variations of the physical constants such as the fine structure constant and the electron-proton mass ratio over cosmological time scales can be investigated using $H_2$ spectra. Such variations could be the key for many questions in cosmology, dealing with the evolution of the universe. In order to address these ideas, the properties of the molecule must be calculated and measured, precisely. One important property is the energy levels or states of the molecule. The Schrödinger equation can be solved to obtain these energy levels; the state energies or *eigenenergies* are solutions to the Schrödinger equation, a conservation of energy relation. These energies are the result of the motion of the electrons and nuclei. These motions correspond to rotational and vibrational degrees of freedom and the combination of the two are called *rovibrational*. The energies to be calculated are hence *rovibrational eigenenergies*. These eigenenergies are also the binding energies for $H_2$; they are the energies needed to dissociate the molecule from a certain state. Therefore the states are the bound states of $H_2$.

There is a helpful approximation that can be used to calculate these states: the Born-Oppenheimer approximation. Although the Born-Oppenheimer approximation is useful for diatomic molecules, however, for a precise and accurate calculation, it cannot stand on its own. So the calculations of the rovibrational eigenenergies are made perturbatively in which the approximation represents the unperturbed state and corrections are added to it. Experiments have no approximations and for a calculation to match the accuracy of measurement, the perturbation method is essential.

### 1.2 The Born-Oppenheimer Approximation

Often for diatomic molecules, the Born-Oppenheimer approximation (I will abbreviate it as BO for now on) is used due its simplicity. It treats the molecule as a single quantum system. The nuclei are much heavier than the electrons. The motions of electrons on the other hand are more rapid than the nuclei. In the BO approximation, this rapid electronic motion can be separated from the slower nuclear motion; the nuclei are considered to be in a fixed position (approximately). The BO approximation is often called the "adiabatic" approximation because the nuclear motion does not change the electronic wave function significantly. For a general diatomic molecule, the Hamiltonian is:

$$H = -\sum_{K=A,B}\frac{\hbar^2}{2M_K}\nabla_K^2 - \frac{\hbar^2}{2m}\sum_i \nabla_i^{\,2} + \sum_{i<j}\frac{e^2}{r_{ij}} + \sum_{A<B}\frac{Z_A Z_B e^2}{r_{AB}} - \sum_{i;K=A,B}\frac{Z_K e^2}{r_{iK}} \tag{1.1}$$

where the subscript A corresponds to the first nucleus and the subscript B corresponds to the second nucleus. $Z_A$ and $Z_B$ are the nuclear charges, $M_K$ is the mass of either A or B, e is the electronic charge, $r_{AB}$ is the separation between A and B, $r_{iK}$ the separation between the electrons and the nuclei, and $r_{ij}$ the electron-electron separation. The first term is the kinetic energy of the nuclei and the second term is the kinetic energy of the electrons. The last three terms are the potential energy of the entire system of electrons and nuclei; they consist of all the Coulomb interactions between the charged particles (Weissbluth, 1978). This is a complicated Hamiltonian, yet the eigenvalue equation $H\Psi = E\Psi$ is simplified by separating the total wave function into an electronic and a nuclear wave function. $\Psi$ is the total wave function and it can be split into an electronic wave function and a nuclear wave function. Using the electronic wave function, an eigenvalue E is the electronic eigenvalue, the first term in equation (1.1), the nuclear kinetic energy term, can be removed. The electronic wave function depends on the nuclear and electronic positions. The nuclear wave function depends only on the nuclear coordinates and is therefore considered a *vibrational* function. In accordance with the Born-Oppenheimer approximation, the electronic wave function does not vary significantly when the nuclear kinetic term acts on it. Its corresponding eigenvalue E represents the eigenvalue of a particular electronic state (Weissbluth, 1978).

The electronic motion provides the eigenvalues, as represented by E in the eigenvalue equation. The positions of the nuclei only depend on the nuclear separation $r_{AB}$ as does the Coulomb repulsion between the nuclei. A potential arises from the motion of the nuclei; it is the result of the Hamiltonian acting on the wave function. This potential is the Born-Oppenheimer potential, denoted as $V_{BO}$, and contains all of the information about the electrons. Using the masses of A and B and the coordinates of A and B from the origin, one can obtain a relation for the center of mass coordinate. So the kinetic energy of the motion about $r_{AB}$ depends on the reduced mass of the nuclei:

$$\mu = \frac{M_A M_B}{M_A + M_B} \tag{1.2}$$

Using all these factors, the nuclear Schrödinger equation for this system can be written

$$-\frac{\hbar^2}{2\mu}\nabla^2 \mathrm{X}(R) + \left[E - V_{BO}\right]\mathrm{X}(R) = 0\,. \tag{1.3}$$

R is the same as $r_{AB}$, and X(R) is the wave function in the preceding expression.

The solutions of this equation are the rovibrational eigenenergies. The Born-Oppenheimer approximation is standard in molecular physics. Since it is a good approximation, it can be used as a term in a perturbation expansion method. Thus the Born-Oppenheimer potential represents the unperturbed state, and corrections can be added to the potential to improve the accuracy and completeness of the calculation of the bound states. The corrections are due to several effects: relativistic, radiative, adiabatic, and non-adiabatic.

### 1.3 The Corrections

The corrections to the BO potential of $H_2$ are reported in two papers by Wolniewicz (1993, 1995). He calculated the relativistic, adiabatic, and radiative corrections to the electronic potential in the first, and then added non-adiabatic corrections in the second. The source code does not calculate these corrections; the corrections were calculated by Wolniewicz and are included. The calculations were made for the ground state of $H_2$, so the corrections are also for the ground state.

The Hamiltonian used (Eq. 1.1) is non-relativistic, and the relativistic corrections are thus added to account for any relativistic effects. The corrections are written as $E_{rel}=\varepsilon_1+\varepsilon_2+\varepsilon_4+\varepsilon_5$, corresponding to the terms as given by Bethe and Salpeter (1957). The first term is the correction due to the variation of mass with velocity without any dependence on electron spin. The second term is the correction for the interaction between electrons; it accounts for the retardation of the electromagnetic field produced by an electron. The third term (denoted with the number 4) is a term characteristic of the Dirac equation, involving the electrons' momentum in an electric field. The fourth term represents the interaction of the spin magnetic dipole moments of the two electrons. A correction for spin-orbit coupling is zero because our calculations are for the Σ ground state.

The radiative corrections are due to quantum electrodynamic (QED) effects. These corrections represent the emission of a virtual photon by either one of the electrons and the interaction of the electrons with the Coulomb potential of the nuclei. The photon is then absorbed by the electron that emits it, and there is a shift in the ground state energy. There is also an exchange of virtual photons between the electrons; this effect due to the interaction of one electron with the other's Coulomb potential.

The adiabatic corrections can be written as

$$E_1^{'} = -\frac{1}{2\mu}\langle \Delta_R \rangle \qquad (1.4),$$

$$E_2^{'} = -\frac{1}{4\mu}\langle \Delta_1 + \nabla_1 \nabla_2 \rangle \qquad (1.5).$$

The expectation values here have been computed with respect to the electronic wave function. It should be noted that the adiabatic correction is mass-dependent, whereas the relativistic and radiative corrections are independent of mass. It is important for $H_2$, since its nuclei are less massive than a molecule such as CO, and the BO approximation is more appropriate for molecules with heavier nuclei.

The last correction, the non-adiabatic correction, is a small addition but does make a difference when comparing to the calculated energies to the measured values. The binding energies where calculated both without the non-adiabatic correction and with the non-adiabatic correction. The equation for the non-adiabatic correction is

$$E_{v,J}^{''} = E_{v,J}^{''}(\Sigma_g) + E_{v,J}^{''}(\Pi_g) + E_{v,J}^{''}(\Sigma_u) + E_{v,J}^{''}(\Pi_u) \qquad (1.6).$$

The subscripts v and J are the vibrational and rotational quantum numbers, respectively. So this correction involves the vibrational and rotational degrees of freedom. It is also involves the coupling of the Σ and Π states. The subscripts g and u correspond to gerade and ungerade states. A gerade state is an even state with respect to the inversion at the center of symmetry of the molecule, midway between the nuclei. An ungerade state is therefore an odd state with respect to the inversion. In this particular calculation the Σ state has the largest non-adiabatic correction and therefore the calculation will be limited to this interaction.

## 1.4 Calculation of Bound States

In the process of calculation, two sources were used in the computation code: the $H_2$ BO potential with adiabatic, relativistic, and radiative corrections (Wolniewicz, 1993) and the addition of the effective local non-adiabatic potential from Williams and Julienne (1993) which does not explicitly depend on the rovibrational state. The total potential is an effective local potential; it is spherically symmetric. Since the potential is spherically symmetric, the differential operator of the nuclear Schrödinger equation mentioned earlier is now depends only on the radial component, R. The BO potential also represents the unperturbed electronic state. The corrections are added to this BO potential in accordance to the perturbative method described earlier. Therefore the radial nuclear Schrödinger equation is

$$\frac{d^2}{dR^2}\mathrm{X}_{vJ}(R) + 2\mu\left[E_{vJ} - V(R) - \frac{J(J+1)}{2\mu R^2}\right]\mathrm{X}_{vJ}(R) = 0 \qquad (1.7).$$

E is the eigenenergy, V(R) is the total interaction potential, and $\mathrm{X}_{vJ}(R)$ are the vibrational eigenfunctions. (This equation is true when energy is expressed in atomic units; therefore Planck's constant is equal to 1.) The reduced mass here is the bare nuclear mass of the molecule which is 1836.1527 atomic units. The nuclear mass is used because all the necessary information about the electrons is contained in the interaction potential. The following figure is a plot of the total interaction potential versus the internuclear separation R. The bound states that were calculated are contained in this potential.

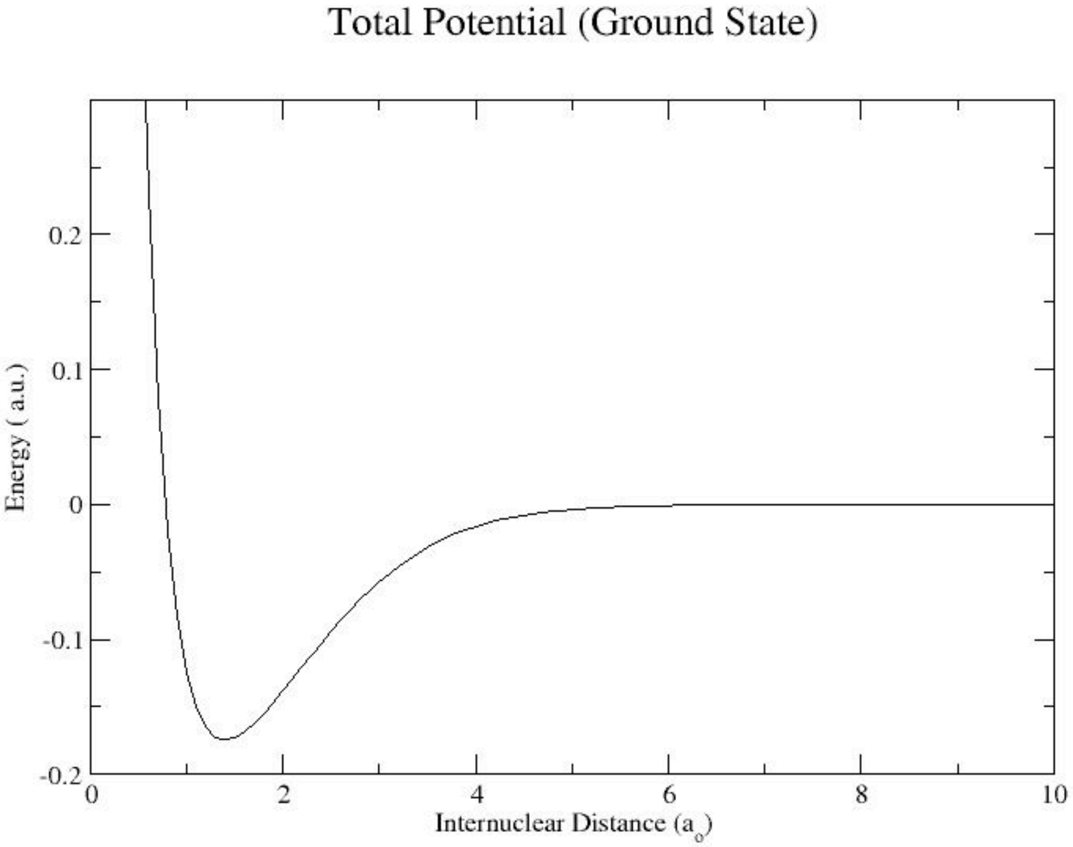


**Figure 1.1 The total potential for the ground state of diatomic hydrogen. The abscissa is in units of Bohr radii $a_0$=0.529177249x$10^{-10}$ m and the ordinate is in units of atomic units or hartrees-1 a.u. =27.2 eV (approximately).**

The code thus uses this equation and solves by using a Numerov-Cooley method. The output of the code lists the levels by their vibrational and rotational quantum numbers. The range of vibrational quantum numbers is v=0, 14 and the range for the rotational numbers is J=0, 31. The calculations of the levels occurred in two phases. First the energies were calculated without the non-adiabatic effects, and then the energies where re-calculated with the non-adiabatic correction, the primary goal is to test the effect of including the non-adiabatic correction. Both results were compared to the experimental values measured by Dabrowski (1984). The calculated values computed, using the non-adiabatic correction, are closer to the experimental energies than the ones without, which was expected. The calculations for the levels are more complete by using all four corrections. There are 301 calculated bound states in all. The dissociation energy (which is also the depth of the total potential well) is 4.476 eV which is the binding energy of the v=0, J=0 state. The last binding energy calculated was for the v=14, J=3 state.

### 1.5 Results

The calculated energies compared well with the experimental values. The calculated energies are plotted versus the vibrational number. The binding energies here are from the calculation that includes the non-adiabatic correction.

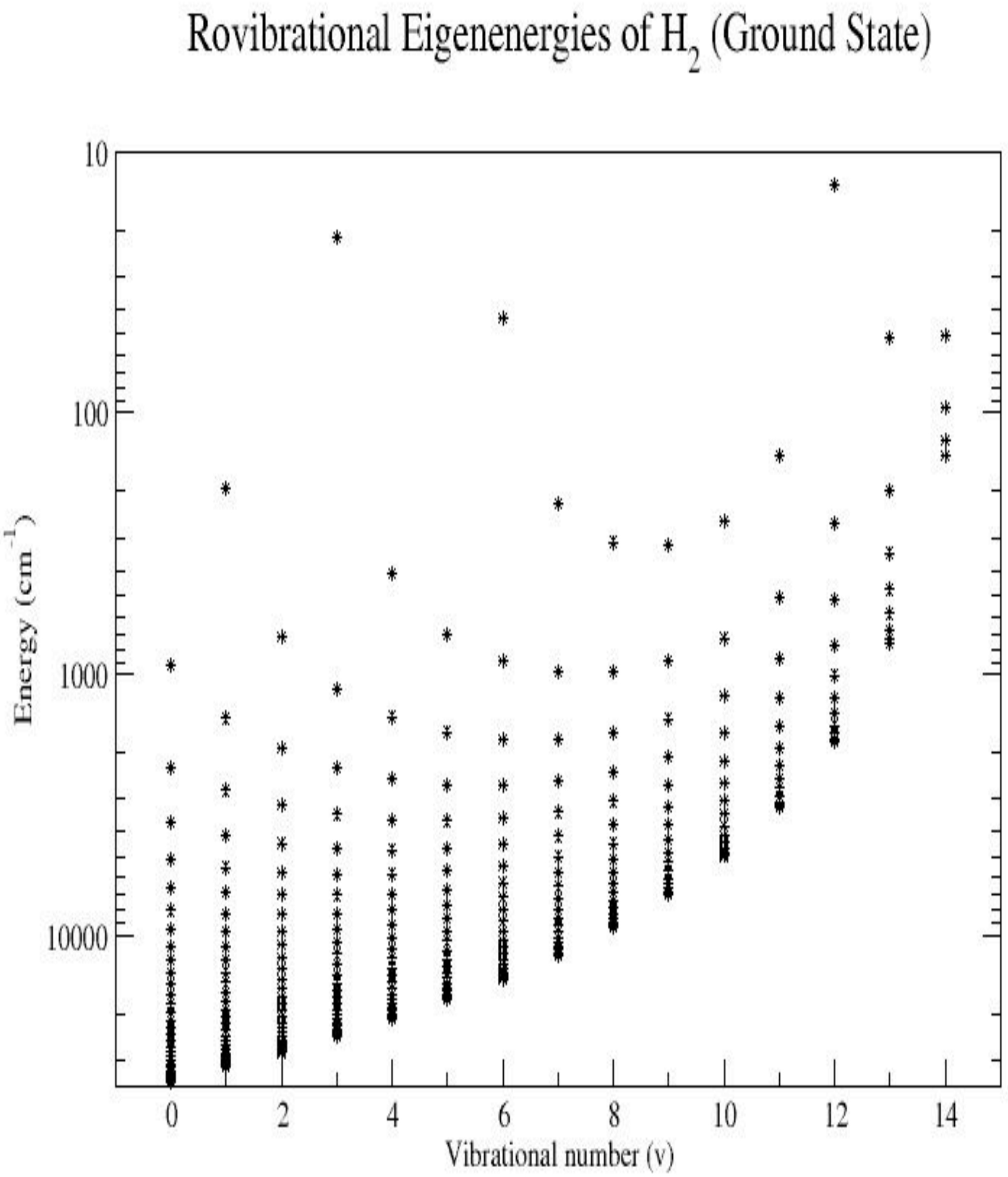
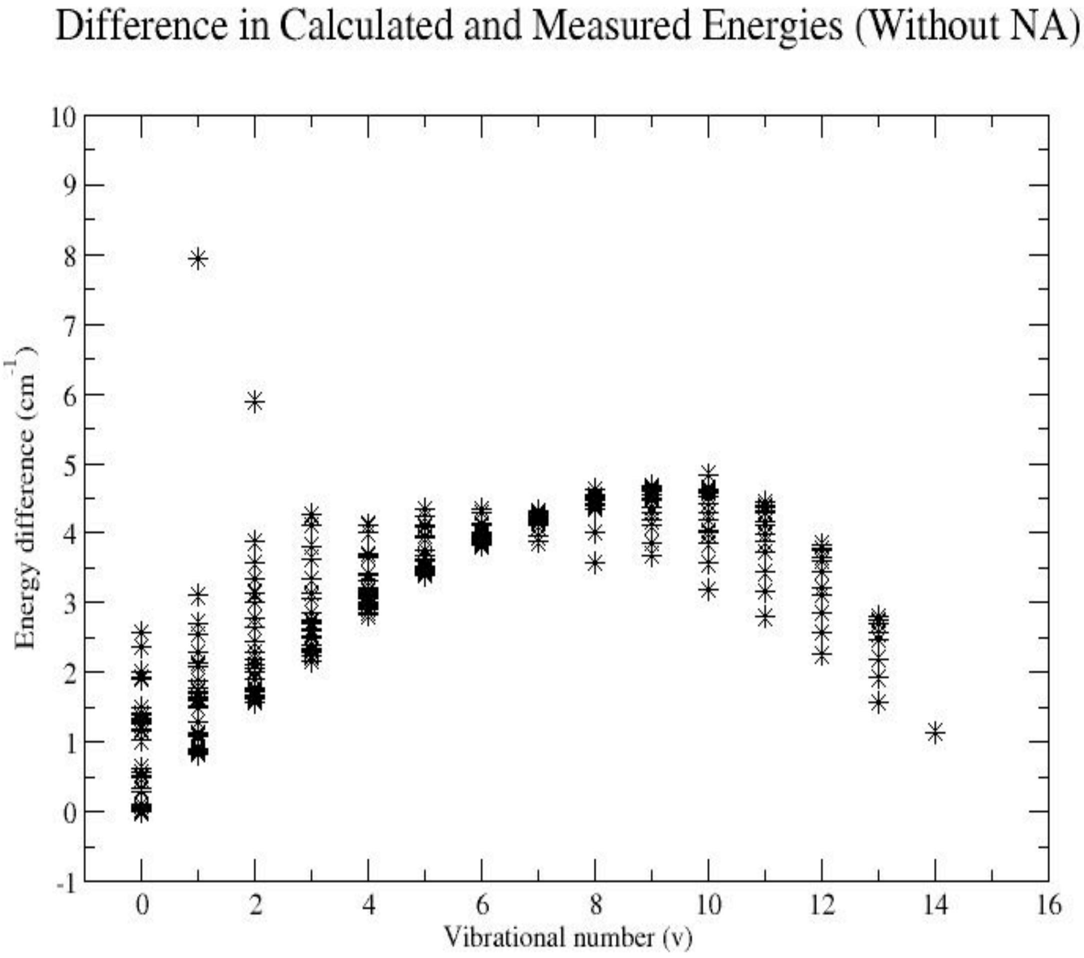


**Figure 1.2 The calculated energies are given in units of corresponding wave numbers. The straight vertical lines of data represent the same vibrational number v but different rotational number J.**

The differences in the calculated energies and measured energies have been plotted and are shown in the following figures. The first graph represents the calculation that excludes the non-adiabatic correction and the second represents the calculation that includes the fourth correction.



Difference in Calculated and Measured Energies (Without NA)

**Figure 1.3 The energy difference is the relative difference between the calculated energies and the measured energies published by Dabrowski (1984). Note the size of the scale for the energy difference.**

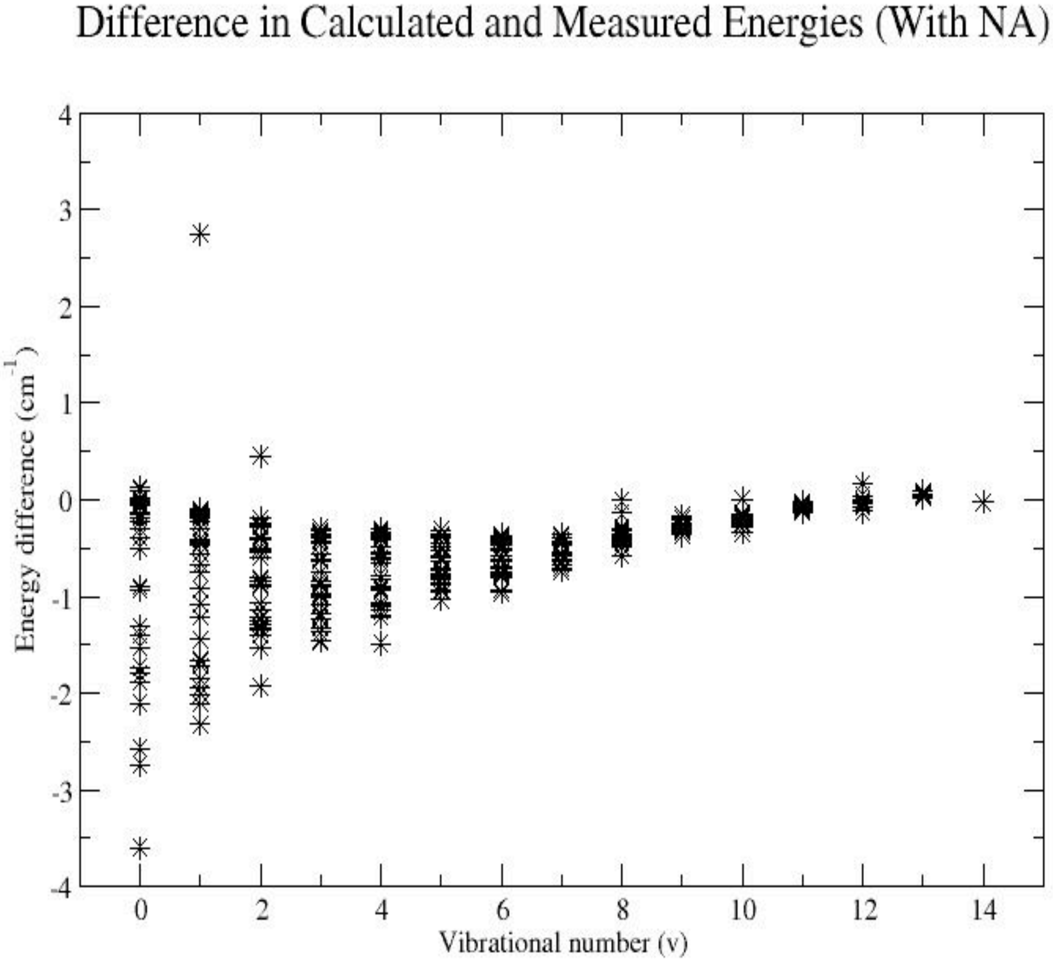


**Figure 1.4 The non-adiabatic correction is small, but the inclusion of it decreases the scale size of the energy difference. Therefore the non-adiabatic correction helps to produce more spectroscopically accurate calculations of the bound states.**

The energy differences decrease from a maximum relative difference of 5 $cm^{-1}$ to maximum relative difference of 4 $cm^{-1}$, though most states lie within 1 $cm^{-1}$ of the measurements. The few states which suggest larger errors where actually obtained not by Dabrowski, but by Roncin and Launay who performed a reanalysis of Dabrowski's UV spectrum (Roueff 2004). These correspond to the v and J pairs: (0,28), (1,28), (1,29), (2,27), and (2,28). Since these levels do not appear in Dabrowski's original assignments, we speculate that they are interpolated or extrapolated values. As such, the values calculated with the non-adiabatic correction appear to be more reliable. With the success of calculating bound states, the next step is to calculate another important property of $H_2$: the transition probabilities due the molecule's quadrupole moment. The binding energies are listed in the Appendix, in both hartrees (a.u.) and corresponding wave numbers.

# Chapter 2

# QUADRUPOLE MOMENT TRANSITION PROBABILITIES

## 2.1 Introduction

Electrons are excited and de-excited in atoms and molecules; they make *transitions* between the energy levels. Due to conservation of energy, these transitions absorb or emit radiation or photons. De-excitation leads to the emission of photons hence there are emission lines or emission spectra generated by this process. For the $X^1\Sigma_g$ ground state of $H_2$, infrared emission is generated. Infrared emission lines are important in the study of galactic environments and quasars, which can generate such emission. Unlike other molecules, i.e. heteronuclear, the transitions between the rovibrational levels in the ground state of $H_2$ are quadrupole moment transitions, as discussed below. The probabilities of these quadrupole moment transitions can be calculated by knowing the rovibrational binding energies, the vibrational wave functions and the quadrupole moment operator.

## 2.2 The Quadrupole Moment

An electric dipole is a system that consists of two equal and opposite charges separated by a distance. The electric dipole moment is the product of the total charge times the distance vector between the charges. An electric quadrupole is a system of two equal and opposite dipoles. Diatomic hydrogen is a quadrupole; it is composed of two electrons in a cloud around two protons. Because the dipole moment is a vector, these two equal and opposite dipoles cancel each other out when added as vectors. The net dipole moment for the molecule is thus zero. However, the next term in the multipole expansion for charge potential, the quadrupole moment, is not a vector but a second-rank tensor or matrix and is non-zero. The equation for the quadrupole moment matrix element is

$$Q(R) = \left\langle \phi(r|R) \middle| \sum_{i=1}^{2} r_i^2 P_2(\cos\theta_i) \middle| \phi(r|R) \right\rangle \qquad (2.1).$$

According to equation (2.1), the matrix element is calculated as an expectation value with respect to the electronic state. The bra and kets correspond to the electronic eigenfunctions. In this calculation, the eigenfunctions correspond to the ground electronic state of $H_2$. The vector R stands for the internuclear distance or separation, which is considered to be fixed, keeping in accordance with the Born-Oppenheimer approximation. The vectors $r_1$ and $r_2$ are the position vectors of the electrons measured from the center of mass and $\theta_1$ and $\theta_2$ are the polar angles of these vectors. The $P_2$ is the second order Legendre polynomial. The quadrupole moment for $H_2$ has been calculated by Wolniewicz, Simbotin, and Dalgarno (1998) and is used in the code to calculate the transition probabilities. The electronic eigenfunction was constructed in that work with a basis of 494 terms. The quadrupole moment is plotted in the following figure. Q(R) and R are expressed in atomic units.

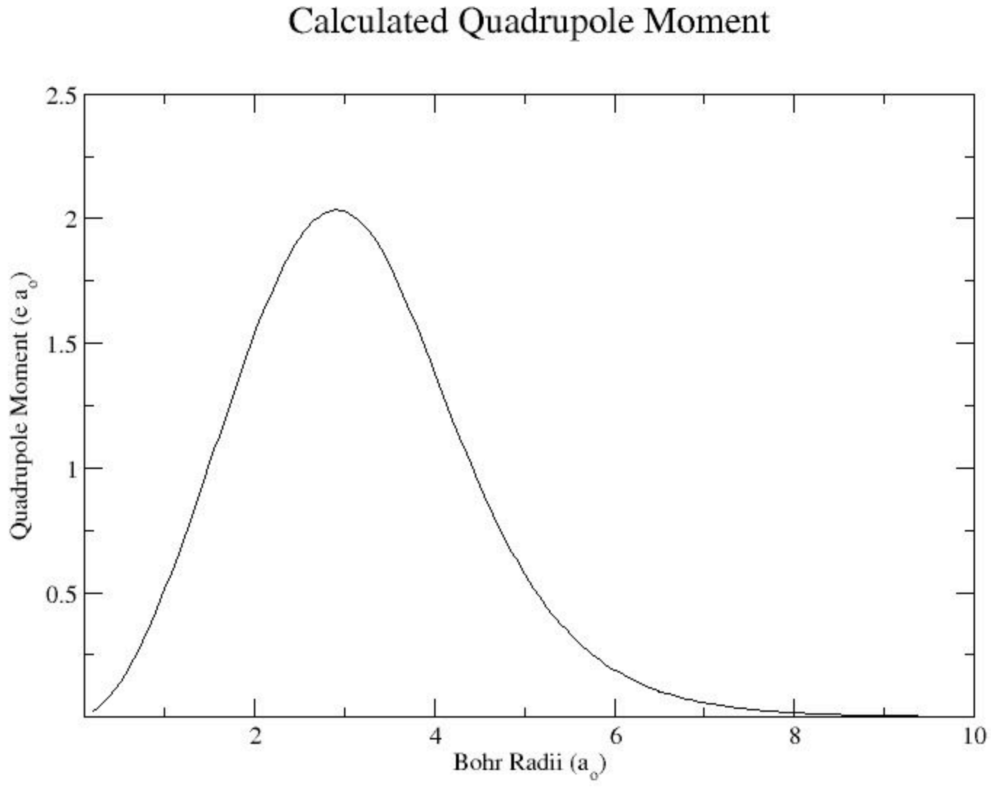


**Figure 2.1 The quadrupole moments calculated by Wolniewicz, Simbotion and Dalgarno (1998). The range of Bohr radii is from 0 to 20, however, the values beyond 8 Bohr are so small ($<10^{-4}$) that they are not noticeable.**

With the quadrupole moment of the ground electronic state intact, the transition probabilities and the transition energies between the rovibrational energy levels can be calculated.

## 2.3 Transition Probabilities

Electrons are excited to higher rovibrational levels and then de-excite, returning to the previous lower level or another lower level. Energy must be conserved, so this process generates a photon. The emission spectra of a molecule are the photons generated by these transitions. The energy of the photon, which is the difference between the energies of the higher and lower bound state, is the transition energy. The emission spectra for the ground state of $H_2$ are infrared emissions. The emission lines are grouped into certain bands or branches. The branches correspond to the selection rules of the transitions. Certain transitions are “allowed” whereas other transitions are “forbidden”. The selection rules define which transitions are allowed. The bound states are rovibrational so the selection rules are based on the rotational quantum number J. For the ground state of $H_2$, there are three selection rules for three branches. The S branch corresponds to the selection rule $\Delta J = J''-J' = -2$. The Q branch corresponds to the $\Delta J = J''-J' = 0$ selection rule. The O branch corresponds to the $\Delta J = J''-J' = 2$ selection rule. There is no selection rule for the vibrational quantum number. For $\Delta v \neq 0$ the transitions generate infrared spectra that are also rovibrational spectra (Dahl 2001). This of course is the emission spectra of interest for this calculation though we also calculated pure rotational transitions.

The probability of the transition is proportional to the fifth power of the transition energy. The transition probability is derived using the time evolution operator from quantum mechanics. The equation for it is

$$A(v'J', v''J'') = 1.4258 \times 10^4 (E_{v'J'} - E_{v''J''})^5 \times \left| \left\langle \mathrm{X}_{v'J'} \middle| Q(R) \middle| \mathrm{X}_{v''J''} \right\rangle \right|^2 f(J', J'') s^{-1} \qquad (2.2).$$

The transition probability is often called the Einstein coefficient. For this expression, the unit for A is reciprocal seconds, same as the unit for frequency. Often it is also called the transition rate. The numerical coefficient is the result of the fine structure constant α to the fifth power divided by 15 and multiplied by a conversion factor to give units of $s^{-1}$ (see Abgrall et. al., 1982). The third term is the square of the expectation value of the quadrupole moment taken with respect to the vibrational eigenfunctions $X_{v'J'}$ for the initial state and $X_{v''J''}$ for the final state. The values for the binding energies and the eigenfunctions from the bound state calculations are used here. The f(J, J”) term represent the angular coefficients of the branches of emission spectra. These coefficients come from using spherical harmonics. For the S branch,

$$f(J',J'')=\frac{3J'(J'-1)}{2(2J'-1)(2J'+1)},\quad J''=J'-2 \qquad (2.3),$$

for the Q branch,

$$f(J',J'')=\frac{J'(J'+1)}{(2J'-1)(2J'+3)},\quad J''=J' \qquad (2.4),$$

and for the O branch,

$$f(J',J'')=\frac{3J'(J'-1)}{2(2J'-1)(2J'+1)},\quad J''=J'+2 \qquad (2.5)\,.$$

These angular coefficients are the Hönl-London factors divided by a factor of (2J’+1). The interaction potential from the bound state calculations is used in these calculations to compute the vibrational eigenfunctions and the rovibrational eigenenergies. The calculations have been done in two phases: without the non-adiabatic correction and with the non-adiabatic correction. Wolniewicz et. al (1998) calculated the transition probabilities without the non-adiabatic correction. Thus the focus is to match the previous calculation and see if the non-adiabatic correction is large enough to make a difference as it did for the calculations of the bound state energies.

## 2.4 Results

The transition probabilities calculated are very small, on the order of $10^{-6}$ $s^{-1}$. The following figures are graphs of the transition probabilities plotted versus the vibrational number.

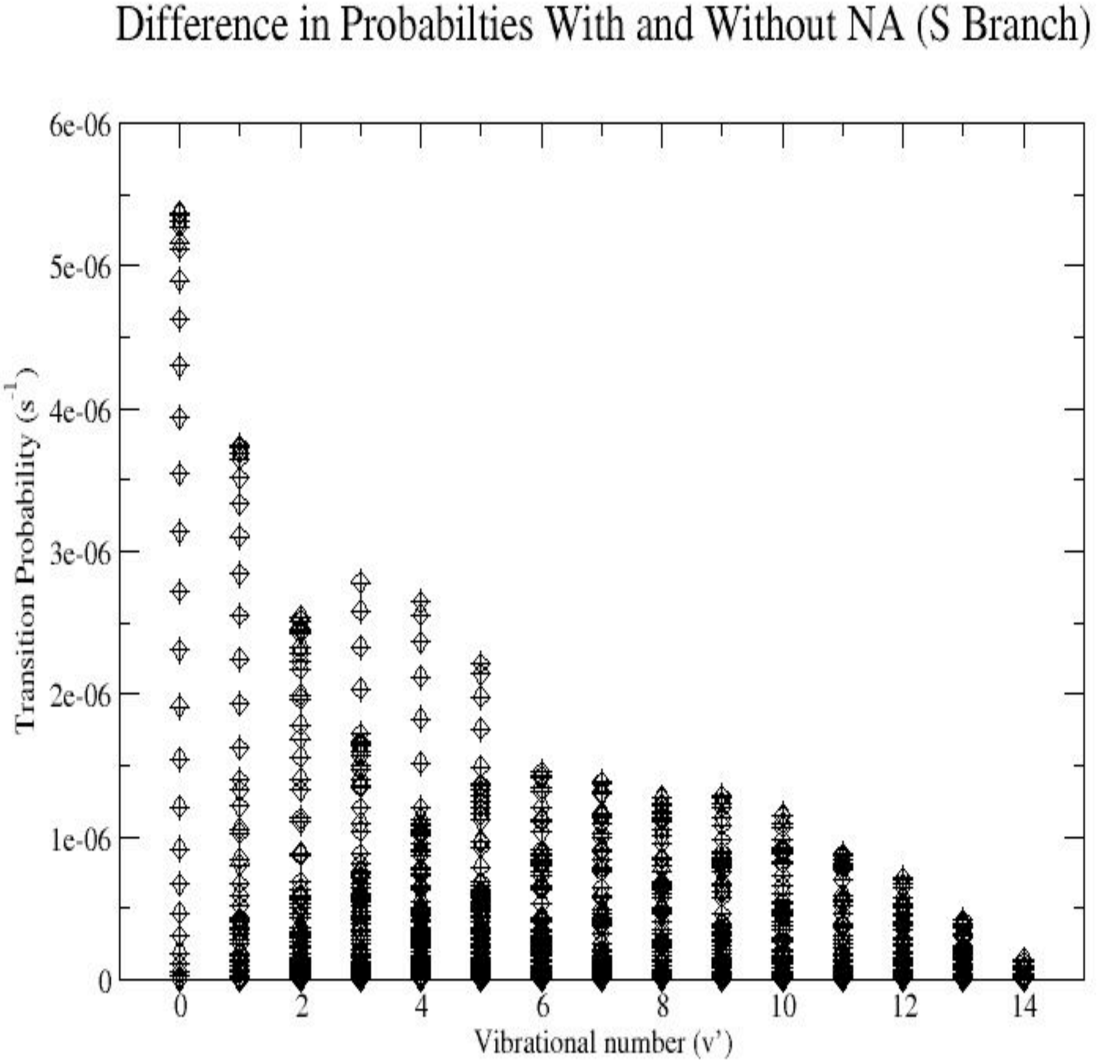


**Figure 2.2The transition probabilities for the S branch. The plus signs denote the first calculation (without the NA correction) and the diamond symbols denote the second calculation. The difference is minimal. The vibrational number is denoted as v' to refer to the initial state.**

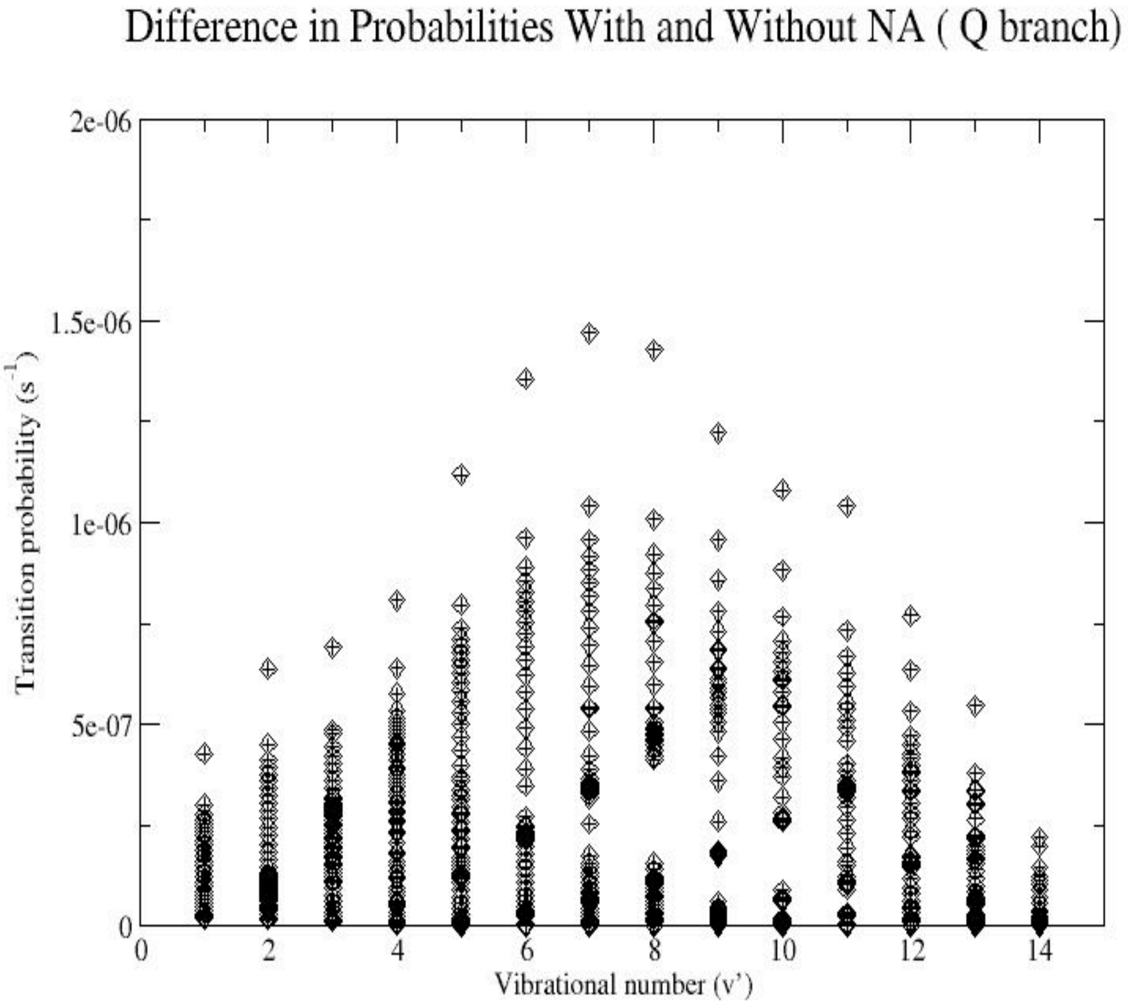


**Figure 2.3 The transition probabilities for the Q branch. The different symbols indicate the different calculations: with and without the non-adiabatic correction. The difference here is also minimal.**

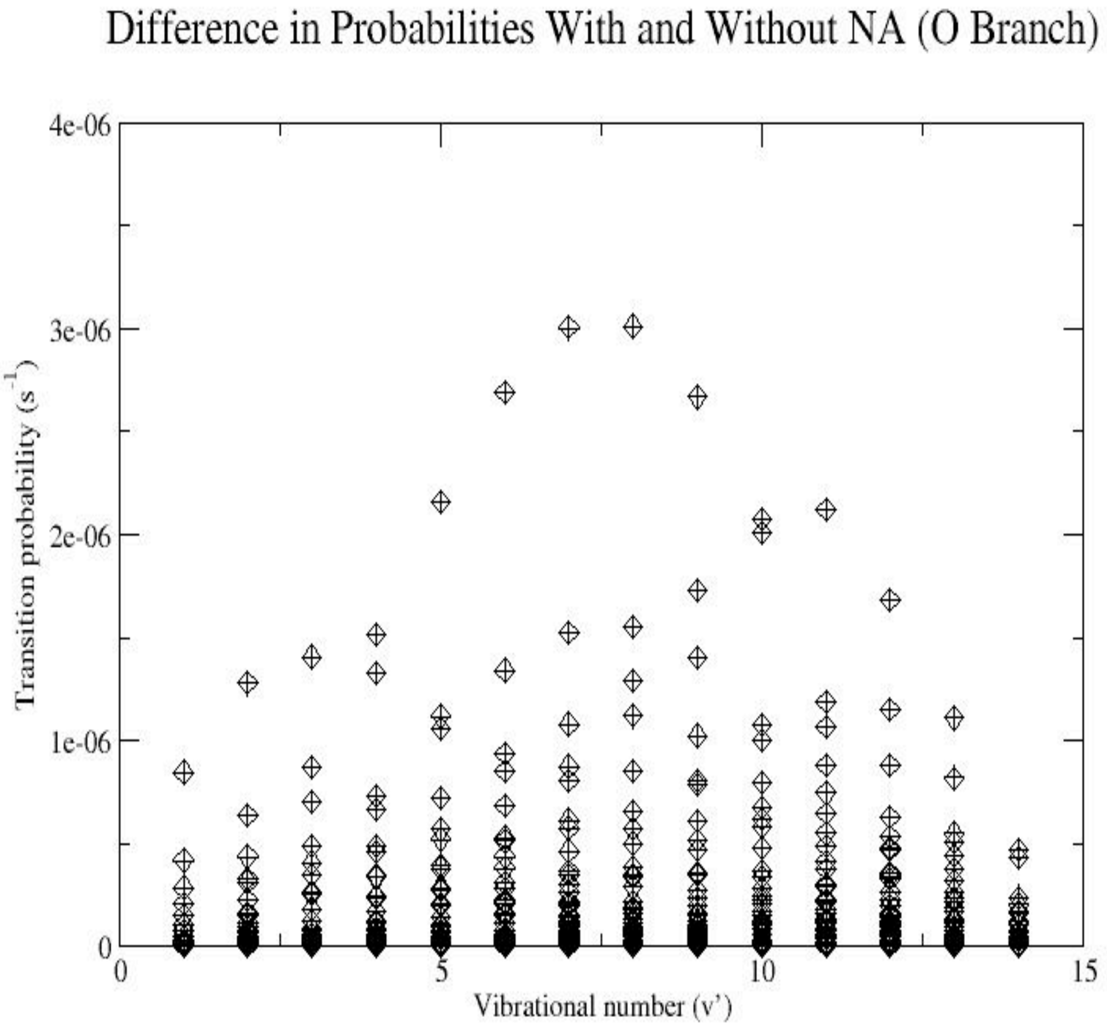


**Figure 2.4 The transition probabilities for the O branch. The symbols refer to the different calculations as the previous plots. It can be concluded that the non-adiabatic correction is too small to give a noticeable effect on the calculated probabilities.**

# Chapter 3

# LTE COOLING FUNCTION

## 3.1 Introduction

The interstellar medium is composed of molecular species such as $H_2$, CO, OH, CH, and CS. $H_2$ is the most plentiful species. Spectroscopic measurements of the interstellar medium include the infrared emission spectra mentioned previously that is the result of vibrationally excited eigenstates of diatomic hydrogen's ground state. The formation of $H_2$ in the interstellar medium (ISM) and other molecular species is possible due to cooling; the energy lost keeps molecules from dissociating into atoms. One important cooling mechanism is radiative; the escape of photons from the gas contributes to cooling. $H_2$ does not have a dipole moment but does have a quadrupole moment. Quadrupole moments are weaker and the transition probabilities associated with the rovibrational transitions are small (Le Bourlot, des Forêts, and Flower 1999). In the previous chapter, the transition probabilities are shown to be very small (around $10^{-6}$ $s^{-1}$). Because the dominant processes that excite molecules in the interstellar medium are usually collisions, the ISM is not generally in local thermodynamic equilibrium or LTE since the density is too low. However, the density is high enough in regions of the ISM that are collapsing, to form stars for example, so LTE is a good approximation. Investigating the properties of the gases that constitute interstellar medium such as its temperature requires knowledge of the *cooling function* that is associated with the radiative cooling. In general, the calculation of the cooling function is not a simple calculation, but it is straight forward for the LTE limit and can be done by combining the previous calculations of the bound states and the transition probabilities.

### 3.2 Radiative Cooling

Radiative cooling of a system occurs when photons are emitted from the system, thus lowering the energy of the system. In the derivation of the cooling function, local thermodynamic equilibrium is assumed. Local thermodynamic equilibrium (LTE) is assumed when collisions dominate other physical processes in a gas. The velocity and energy distribution of the gas particles can be explained by Maxwell and Boltzmann distributions. A temperature can be defined for the gas. As will be seen below, in the LTE limit the cooling function therefore depends on temperature. However, the cooling function is derived below starting with an arbitrary density.

To derive the cooling function, consider two atoms, species A and species B. Consider atom A to be a two-level system with energy levels denoted as level 1 and level 2. Species A can be excited from level 1 to level 2 by either colliding with B or absorbing a photon. The de-excitation from level 2 to level 1 can occur by stimulated or spontaneous emission of a photon or by the collision of A with B. The excitation can be considered as a forward process and de-excitation is then the reverse process. If neither process dominates, there is equilibrium, or detailed balance of the processes. The equation for this situation is

$$n_B n_1 q_{12} + n_1 B_{12} = n_B n_2 q_{12} + n_2 A_{21} + n_2 B_{21} \tag{3.1}$$

where $n_B$, $n_1$, $n_2$ are the number densities in units of $cm^{-3}$, $q_{12}$ is the collisional rate coefficient for excitation, and $q_{21}$ is the collisional rate coefficient for de-excitation, and steady-state is assumed. The rate coefficients are in units of $cm^3/s$ and

$$q_{21} = q_{12} \frac{g_1}{g_2} e^{\frac{-\Delta E}{kT}} \qquad (3.2).$$

In this equation for $q_{21}$, $g_1$ and $g_2$ are the degeneracies of the energy levels. In equation (3.2), ΔE is the difference in the energy levels, k is Boltzmann's constant, and T is the absolute temperature. $A_{21}$ is the Einstein coefficient for spontaneous emission from atom A; as noted in Chapter 2, this is also the transition probability. $B_{12}$ and $B_{21}$ are the Einstein coefficients for absorption and stimulated emission, respectively. Solving for $n_2$, the number density in the upper state, gives

$$n_2 = \frac{n_1\left(n_B q_{12} + B_{21}\right)}{n_B q_{21} + A_{21} + B_{21}} \qquad (3.3).$$

The cooling rate per volume is defined as $\Lambda = n_2 A_{21} h\upsilon_{21}$, with $h\upsilon_{21}$ representing the energy of the emitted photon. Using equation (3.3), this equation becomes

$$\Lambda = \frac{n_1 A_{21} h\upsilon_{21}(n_B q_{12} + B_{12})}{n_B q_{21} + A_{21} + B_{21}} \qquad (3.4).$$

In the limit of a small radiation field, $B_{12}=0$ and $B_{21}=0$ so these terms vanish. Now dividing through the denominator by $A_{21}$, the equation becomes

$$\Lambda = n_B n_1 q_{12} h\upsilon_{21} \frac{1}{\left[1 + \frac{n_B q_{21}}{A_{21}}\right]} \qquad (3.5).$$

Now there are two additional limits that can be considered. If the density of B is low, $n_B$ approaches zero, and $\Lambda \rightarrow n_B n_1 q_{12} h\upsilon_{21}$ with the denominator being reduced to 1. The density $n_1$ is approximately $n_A$ here as well. Now if $n_B$ goes to infinity, the LTE limit

$$\Lambda = \frac{n_B n_1 q_{12} h\upsilon_{21} A_{21}}{n_B q_{21}} = n_1 A_{21} h\upsilon_{21} \frac{q_{12}}{q_{21}} \qquad (3.6).$$

Applying equation 3.2 for $q_{21}$ to equation (3.7), the cooling rate per volume becomes

$$\Lambda = n_1 \frac{g_2}{g_1} e^{\frac{-\Delta E}{kT}} A_{21} h\upsilon_{21} \qquad (3.7)$$

$$n_2 = n_1 \frac{g_2}{g_1} e^{\frac{-\Delta E}{kT}} \tag{3.8}$$

## 3.3 The $H_2$ Cooling Function

Now that the LTE cooling function is defined, it can be applied to the $H_2$ molecule and calculated. Equation (3.7) is the cooling function and its units are ergs/s. For this thesis, quantities like the number density of $H_2$ molecules in a gas are not considered. Thus instead of calculating the cooling function, the focus is to calculate the cooling function divide by the number density, $\Lambda/n_1$. The actual calculation is referred to as the cooling rate coefficient. The energy levels correspond to the rovibrational eigenenergies, the Einstein coefficients are the quadrupole transition probabilities, and the energies of the emitted photons are the transition energies. The energy levels are labeled according to the vibrational and rotational numbers, with v' and J' representing energy level 1 and v'' and J'' representing level 2. (The minus sign on the energy difference compensates for the fact energy level 2 is higher in value.) This calculation applies to the Σ ground electronic state. The degeneracies $g_1$ and $g_2$ also have to be applied. Diatomic hydrogen exists in two forms: ortho-$H_2$ and para-$H_2$. These forms are a consequence of $H_2$ being homonuclear (Le Bourlot et. al., 1999). The differences between the two forms are the total nuclear spin number I and the rotational quantum number J. Ortho-$H_2$ has a total nuclear spin I=1 and odd values for J. Para-$H_2$ has a total nuclear spin I=0 and even values for J. Using the notation change, the degeneracies $g_1$ and $g_2$ can be written as $g_{J'} = (2I+1)(2J'+1)$ and $g_{J''} = (2I+1)(2J''+1)$, respectively. In order to account for all the rovibrational eigenenergies, transition probabilities, and the degeneracies, the cooling rate coefficient is calculated as a sum over all possible states:

$$\frac{\Lambda}{n_1} = \sum_{vJ}^{v'J'} A(v'J', v''J'') \times h\upsilon \times \exp^{\frac{-(E(v'J')-E(v'',J''))}{kT}} \times \frac{((2I+1)(2J'+1))}{((2I+1)(2J''+1))} \quad (3.9).$$

### 3.4 Calculation

The cooling rate coefficient depends on temperature. When using equation (3.9), a single temperature has to be defined in accordance with LTE. Since the coefficient includes the transition probabilities, the selection rules used to define the different branches of emission spectra are programmed into the code. Therefore, the selection rules are the same as the selection rules mentioned in Chapter 2 that define the S, Q, and O branches. So for a single temperature, the cooling rate coefficient is calculated using the allowed transitions between levels and for both forms of $H_2$. The temperature is absolute temperature, in units of K. Energy is in units of cm$^{-1}$, transition probability is in s$^{-1}$ and Boltzmann's constant in units of ergs/K. The range of temperature is from 10 K to $10^9$ K. The cooling rate coefficient has units of ergs/(s cm$^{-3}$), so the energy is converted into units of ergs.

### 3.5 Results

This calculation must match the cooling function curve for $H_2$ calculated by Le Bourlot et. al. (1999). The following plot is of the calculated cooling rate coefficients as a function of the temperature.

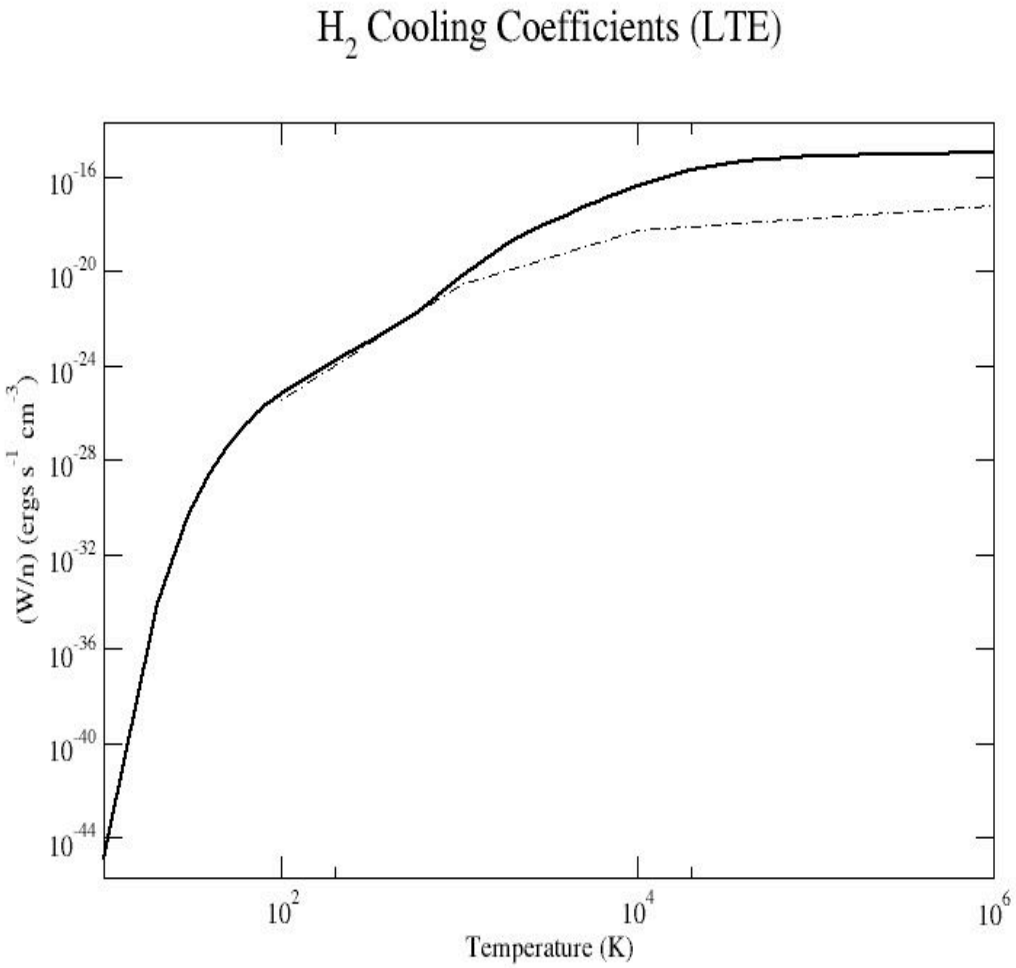


**Figure 3.1 The cooling rate coefficients are plotted here as a function of temperature. Both axes are logarithmic scales. W is analogous to Λ, the cooling function. The dashed line is the cooling function calculated by Le Bourlon et. al (1999). Note that the curve flattens around temperatures between $10^4$ and $10^5$ K.**

The new cooling function is in agreement with that figure calculated by Le Bourlot et. al. (1999) for T<1000 K. The figure only ranges from 10 K (where the rate coefficient is practically zero) to $10^6$ K. Beyond this range, the cooling rate is constant. The rate coefficients increase with increasing temperature within the range shown in the figure. However, for larger temperature, the current LTE cooling function is larger than that obtained by Le Bourlot et. al. who considered a limited set of rovibrational states with

$v_{max}$=3 and $J_{max}$=16. In the current calculation all 301 rovibrational levels ($v_{max}$=14, $J_{max}$=31) are included. Therefore, the current cooling function can be used in the study of high density gases and is more reliable at higher temperatures.

# Chapter 4

# CONCLUSION AND FUTURE WORK

## 4.1 Summary

The rovibrational eigenenergies for the bound states of $H_2$ in its $\Sigma$ ground state have been calculated by using a perturbative method that involves the Born-Oppenheimer approximation and corrections to the approximation. These energies are solutions to the radial nuclear Schrödinger equation. The calculations have been done before; however, corrections for non-adiabatic effects have been included in only a few calculations performed by others. The calculated energies compared well with the measured energies, the difference being no more than 5 $cm^{-1}$, when the non-adiabatic corrections were considered. The calculated rovibrational eigenenergies were then used to calculate the quadrupole transition probabilities. $H_2$ does not have a dipole moment, but does have a quadrupole moment and therefore the transitions between the levels are quadrupole transitions. The emission lines produced by de-excitation between the levels are infrared spectra, grouped into three branches labeled S, Q, and O. Each branch corresponds to a selection rule for allowed transitions (referring to the rotational number). The transition probabilities where calculated for each branch, with and without the non-adiabatic corrections. The non-adiabatic corrections are too small to make a noticeable difference in the calculated probabilities for each branch, as shown in the figures provided in Chapter 2. With the rovibrational energies and transition probabilities, cooling rate coefficients can be calculated. The cooling rate coefficient is the cooling function divided by the number density of the gas. The local thermodynamic equilibrium limit was used, so the cooling rate coefficients depend on temperature. In the local thermodynamic equilibrium (LTE) limit, the number density is high (n goes to infinity). This calculation successfully matches the calculation done by Le Bourlot et. al. (1999) for low temperature, but are larger than the previous results due to inclusion of more highly excited rovibrational levels neglected in the other calculation. The research for this thesis has been successful and future calculations or comparisons can be made.

### 4.2 Future Work

For this thesis, the calculations were made for the ground electronic state of diatomic hydrogen. Others have performed calculations for the excited electronic states. Using these calculations, the emission lines of $H_2$ from quasars can be investigated by calculating the transition energies related to the spectra. Quasar emission spectra are important for exploring the possible cosmological variation of the electron-proton mass ratio. The cosmological variation of the fine structure constant is another possibility. Another future research topic is exploring the possibility of $H_2$ maser lines from protogalaxies. The calculations in this thesis can possibly be used in the study of the early universe. Maser lines from protogalaxies have not been detected as of this writing.

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# APPENDIX

## The Rovibrational Energy Levels

| v | J | a.u. | cm-1 |
|---|---|---|---|
| 0 | 0 | 0.16456618E+00 | 0.36118097E+05 |
| 0 | 1 | 0.16402632E+00 | 0.35999611E+05 |
| 0 | 2 | 0.16295155E+00 | 0.35763726E+05 |
| 0 | 3 | 0.16135163E+00 | 0.35412584E+05 |
| 0 | 4 | 0.15924080E+00 | 0.34949312E+05 |
| 0 | 5 | 0.15663739E+00 | 0.34377929E+05 |
| 0 | 6 | 0.15356327E+00 | 0.33703236E+05 |
| 0 | 7 | 0.15004325E+00 | 0.32930683E+05 |
| 0 | 8 | 0.14610455E+00 | 0.32066238E+05 |
| 0 | 9 | 0.14177610E+00 | 0.31116254E+05 |
| 0 | 10 | 0.13708803E+00 | 0.30087341E+05 |
| 0 | 11 | 0.13207110E+00 | 0.28986252E+05 |
| 0 | 12 | 0.12675626E+00 | 0.27819779E+05 |
| 0 | 13 | 0.12117423E+00 | 0.26594665E+05 |
| 0 | 14 | 0.11535517E+00 | 0.25317531E+05 |
| 0 | 15 | 0.10932846E+00 | 0.23994820E+05 |
| 0 | 16 | 0.10312244E+00 | 0.22632756E+05 |
| 0 | 17 | 0.96764305E-01 | 0.21237307E+05 |
| 0 | 18 | 0.90280033E-01 | 0.19814174E+05 |
| 0 | 19 | 0.83694313E-01 | 0.18368776E+05 |
| 0 | 20 | 0.77030553E-01 | 0.16906250E+05 |
| 0 | 21 | 0.70310907E-01 | 0.15431458E+05 |
| 0 | 22 | 0.63556325E-01 | 0.13948999E+05 |
| 0 | 23 | 0.56786633E-01 | 0.12463224E+05 |
| 0 | 24 | 0.50020626E-01 | 0.10978257E+05 |
| 0 | 25 | 0.43276186E-01 | 0.94980236E+04 |
| 0 | 26 | 0.36570419E-01 | 0.80262781E+04 |
| 0 | 27 | 0.29919817E-01 | 0.65666398E+04 |
| 0 | 28 | 0.23340445E-01 | 0.51226349E+04 |
| 0 | 29 | 0.16848181E-01 | 0.36977478E+04 |
| 0 | 30 | 0.10459008E-01 | 0.22954865E+04 |
| 0 | 31 | 0.41894117E-02 | 0.91946946E+03 |
| 1 | 0 | 0.14560718E+00 | 0.31957078E+05 |
| 1 | 1 | 0.14509427E+00 | 0.31844506E+05 |
| 1 | 2 | 0.14407323E+00 | 0.31620414E+05 |
| 1 | 3 | 0.14255348E+00 | 0.31286869E+05 |
| 1 | 4 | 0.14054880E+00 | 0.30846892E+05 |
| 1 | 5 | 0.13807687E+00 | 0.30304366E+05 |
| 1 | 6 | 0.13515878E+00 | 0.29663919E+05 |
| 1 | 7 | 0.13181848E+00 | 0.28930808E+05 |

```
1   8  0.12808217E+00  0.28110784E+05
1   9  0.12397773E+00  0.27209963E+05
1  10  0.11953416E+00  0.26234712E+05
1  11  0.11478107E+00  0.25191529E+05
1  12  0.10974825E+00  0.24086952E+05
1  13  0.10446528E+00  0.22927475E+05
1  14  0.98961248E-01  0.21719480E+05
1  15  0.93264488E-01  0.20469186E+05
1  16  0.87402412E-01  0.19182609E+05
1  17  0.81401390E-01  0.17865537E+05
1  18  0.75286682E-01  0.16523514E+05
1  19  0.69082410E-01  0.15161834E+05
1  20  0.62811571E-01  0.13785544E+05
1  21  0.56496083E-01  0.12399455E+05
1  22  0.50156859E-01  0.11008157E+05
1  23  0.43813918E-01  0.96160420E+04
1  24  0.37486513E-01  0.82273374E+04
1  25  0.31193307E-01  0.68461387E+04
1  26  0.24952583E-01  0.54764582E+04
1  27  0.18782510E-01  0.41222839E+04
1  28  0.12701500E-01  0.27876566E+04
1  29  0.67286952E-02  0.14767777E+04
1  30  0.88470015E-03  0.19416921E+03
2   0  0.12772026E+00  0.28031353E+05
2   1  0.12723369E+00  0.27924564E+05
2   2  0.12626520E+00  0.27712003E+05
2   3  0.12482388E+00  0.27395671E+05
2   4  0.12292305E+00  0.26978487E+05
2   5  0.12057980E+00  0.26464203E+05
2   6  0.11781451E+00  0.25857292E+05
2   7  0.11465029E+00  0.25162827E+05
2   8  0.11111245E+00  0.24386360E+05
2   9  0.10722787E+00  0.23533793E+05
2  10  0.10302453E+00  0.22611269E+05
2  11  0.98531030E-01  0.21625058E+05
2  12  0.93776117E-01  0.20581476E+05
2  13  0.88788393E-01  0.19486797E+05
2  14  0.83596006E-01  0.18347200E+05
2  15  0.78226442E-01  0.17168717E+05
2  16  0.72706365E-01  0.15957200E+05
2  17  0.67061525E-01  0.14718301E+05
2  18  0.61316708E-01  0.13457460E+05
2  19  0.55495738E-01  0.12179905E+05
2  20  0.49621518E-01  0.10890663E+05
2  21  0.43716107E-01  0.95945751E+04
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2  24  0.26023490E-01  0.57114951E+04
2  25  0.20202192E-01  0.44338681E+04
2  26  0.14453287E-01  0.31721295E+04
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3   2  0.10950576E+00  0.24033732E+05
3   3  0.10814170E+00  0.23734356E+05
3   4  0.10634321E+00  0.23339634E+05
3   5  0.10412684E+00  0.22853197E+05
3   6  0.10151230E+00  0.22279372E+05
3   7  0.98521953E-01  0.21623066E+05
3   8  0.95180254E-01  0.20889648E+05
3   9  0.91513226E-01  0.20084829E+05
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5  21  0.12063903E-01  0.26477202E+04
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6   4  0.62812086E-01  0.13785658E+05
```

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6   7  0.56351476E-01  0.12367718E+05
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7   9  0.39105233E-01  0.85826053E+04
7  10  0.36125097E-01  0.79285411E+04
7  11  0.32963028E-01  0.72345474E+04
7  12  0.29645855E-01  0.65065122E+04
7  13  0.26200996E-01  0.57504532E+04
7  14  0.22656442E-01  0.49725136E+04
7  15  0.19040872E-01  0.41789877E+04
7  16  0.15383932E-01  0.33763823E+04
7  17  0.11716758E-01  0.25715307E+04
7  18  0.80728705E-02  0.17717900E+04
7  19  0.44897462E-02  0.98538524E+03
7  20  0.10117698E-02  0.22205777E+03
8   0  0.42316333E-01  0.92873602E+04
8   1  0.41988158E-01  0.92153342E+04
8   2  0.41335785E-01  0.90721549E+04
8   3  0.40367045E-01  0.88595410E+04
8   4  0.39093389E-01  0.85800060E+04
8   5  0.37529573E-01  0.82367881E+04
```

```
  8   6  0.35693272E-01  0.78337666E+04
  8   7  0.33604677E-01  0.73753731E+04
  8   8  0.31286096E-01  0.68665033E+04
  8   9  0.28761585E-01  0.63124373E+04
  8  10  0.26056650E-01  0.57187728E+04
  8  11  0.23198024E-01  0.50913771E+04
  8  12  0.20213560E-01  0.44363629E+04
  8  13  0.17132249E-01  0.37600935E+04
  8  14  0.13984430E-01  0.30692271E+04
  8  15  0.10802235E-01  0.23708161E+04
  8  16  0.76204394E-02  0.16724929E+04
  8  17  0.44780003E-02  0.98280732E+03
  8  18  0.14210244E-02  0.31187876E+03
  9   0  0.31868583E-01  0.69943445E+04
  9   1  0.31570032E-01  0.69288201E+04
  9   2  0.30976887E-01  0.67986399E+04
  9   3  0.30096950E-01  0.66055160E+04
  9   4  0.28941651E-01  0.63519572E+04
  9   5  0.27525759E-01  0.60412048E+04
  9   6  0.25867039E-01  0.56771581E+04
  9   7  0.23985898E-01  0.52642954E+04
  9   8  0.21905047E-01  0.48076014E+04
  9   9  0.19649218E-01  0.43125042E+04
  9  10  0.17244977E-01  0.37848344E+04
  9  11  0.14720656E-01  0.32308102E+04
  9  12  0.12106474E-01  0.26570635E+04
  9  13  0.94349053E-02  0.20707221E+04
  9  14  0.67414678E-02  0.14795810E+04
  9  15  0.40662348E-02  0.89243526E+03
  9  16  0.14568892E-02  0.31975018E+03
 10   0  0.22635349E-01  0.49678842E+04
 10   1  0.22368892E-01  0.49094036E+04
 10   2  0.21839975E-01  0.47933197E+04
 10   3  0.21056495E-01  0.46213658E+04
 10   4  0.20030059E-01  0.43960891E+04
 10   5  0.18775734E-01  0.41207968E+04
 10   6  0.17311768E-01  0.37994933E+04
 10   7  0.15659309E-01  0.34368206E+04
 10   8  0.13842189E-01  0.30380090E+04
 10   9  0.11886796E-01  0.26088499E+04
 10  10  0.98221167E-02  0.21557051E+04
 10  11  0.76800388E-02  0.16855735E+04
 10  12  0.54960905E-02  0.12062523E+04
 10  13  0.33109798E-02  0.72667596E+03
 10  14  0.11738852E-02  0.25763799E+03
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11   0  0.14721803E-01  0.32310619E+04
11   1  0.14491016E-01  0.31804100E+04
11   2  0.14033581E-01  0.30800147E+04
11   3  0.13357696E-01  0.29316750E+04
11   4  0.12475475E-01  0.27380498E+04
11   5  0.11402769E-01  0.25026182E+04
11   6  0.10158994E-01  0.22296412E+04
11   7  0.87670172E-02  0.19241376E+04
11   8  0.72531808E-02  0.15918889E+04
11   9  0.56475837E-02  0.12395012E+04
11  10  0.39848246E-02  0.87456778E+03
11  11  0.23056702E-02  0.50603604E+03
11  12  0.66092382E-03  0.14505599E+03
12   0  0.82739068E-02  0.18159124E+04
12   1  0.80840222E-02  0.17742375E+04
12   2  0.77087120E-02  0.16918665E+04
12   3  0.71568577E-02  0.15707485E+04
12   4  0.64417122E-02  0.14137922E+04
12   5  0.55808818E-02  0.12248618E+04
12   6  0.45964221E-02  0.10087979E+04
12   7  0.35151883E-02  0.77149454E+03
12   8  0.23697191E-02  0.52009315E+03
12   9  0.12003316E-02  0.26344230E+03
12  10  0.60717800E-04  0.13326015E+02
13   0  0.34933079E-02  0.76669236E+03
13   1  0.33523444E-02  0.73575444E+03
13   2  0.30756028E-02  0.67501670E+03
13   3  0.26735400E-02  0.58677413E+03
13   4  0.21621229E-02  0.47453105E+03
13   5  0.15634012E-02  0.34312685E+03
13   6  0.90688055E-03  0.19903725E+03
13   7  0.23326474E-03  0.51195687E+02
14   0  0.65948555E-03  0.14474033E+03
14   1  0.58130227E-03  0.12758108E+03
14   2  0.43236701E-03  0.94893577E+02
14   3  0.22868952E-03  0.50191541E+02
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