Mass effects in the theoretical determination of nuclear-spin relaxation rates for atomic hydrogen and deuterium

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The normal method for calculating very precise eigenvalues for H_2 and its isotopes is to solve the Schrödinger equation using a reduced mass calculated from the bare nuclear mass with the mass-independent Born-Oppenheimer potentials and with mass-dependent adiabatic and nonadiabatic correction terms that account for the finite mass of the nuclei. On the other hand, scattering calculations have used reduced masses calculated from the masses of the separated atoms to solve the Schrödinger equation with mass-dependent adiabatic potentials, but with no explicit treatment of electronically off-diagonal nonadiabatic corrections. We have extended the conventional bound-state methods based on bare nuclear masses into the continuum by introducing an effective local potential to account for the electronically off-diagonal nonadiabatic mass-dependent corrections. Good agreement is found with previously calculated eigenvalues of H_2 and D_2. The scattering length for the ground state $X\,^1\Sigma_g^+$ of H_2 is very sensitive to the nonadiabatic corrections, but is in good agreement with that previously calculated using a reduced mass based on the separated atomic masses. Using quantum close-coupling methods, we also find good agreement with previously calculated collision-rate coefficients in the $T \rightarrow 0$ limit for collisions of H with H and D with D.

I. INTRODUCTION

One of the most carefully studied theoretical molecular systems is the H_2 molecule and its isotopic analogs. Kolos, Szalewicz, and Monkhorst [1] have produced highly accurate Born-Oppenheimer (clamped-nuclei) *ab initio* potentials for the H_2 molecule and its isotopic analogs. The clamped-nuclei potential originally used by Kolos and Wolniewicz [2] is independent of the nuclear masses and thus gives an isotope-independent Born-Oppenheimer potential $V_{BO}(R)$. In order to obtain effective adiabatic isotope-dependent potentials $V_{ABO}(R)$ from the *ab initio* data of Kolos, Szalewicz, and Monkhorst [1], it is necessary to add mass-independent relativistic and radiative corrections [3–5] along with mass-dependent adiabatic corrections [3,6]. To obtain accurate rovibrational levels for the six isotopes of diatomic hydrogen, one takes the appropriate $V_{ABO}(R)$, calculates its eigenvalues, and adds on nonadiabatic corrections [6] due to electronically off-diagonal interactions. The eigenvalues for total angular momentum $J=0$ are calculated from the Schrödinger equation for the V_{ABO} potential:

$$\left\{ \frac{1}{2\mu}\frac{d^2}{dR^2} + [E - V_{ABO}(R)] \right\}\chi(R) = 0 \ ,$$

where μ is the reduced mass calculated from the bare nuclear masses of the two nuclei. Schwartz and LeRoy [7] describe a recipe for preparing the effective adiabatic potentials $V_{ABO}(R)$ based on Refs. [1–6] and on the large-R results of Deal [8] and of Bukta and Meath [9]. The calculations presented in this paper use the $V_{ABO}(R)$ poten-

tials described in detail by Schwartz and LeRoy [7] using programs and input decks provided to us by LeRoy.

Full close-coupling calculations of the nuclear-spin relaxation rates and spin-exchange frequency shifts for atomic hydrogen and deuterium in specific Zeeman sublevels of the two hyperfine components have been made by Verhaar and collaborators [10–16]. They also developed approximations based on the degenerate-internal-state approximation (DIS) [16]. In these calculations the Schrödinger equation (1) was solved using the reduced mass obtained from the atomic masses [12], with no explicit attempt to investigate effects associated with the R-dependent nonadiabatic interactions. The justification for this was twofold: (1) use of the atomic mass is asymptotically correct, as shown by the fact that the bound-state energies nearest the continuum can be fairly accurately reproduced by replacing the reduced mass obtained using the bare nuclear mass by one obtained using the atomic mass and neglecting nonadiabatic interactions (see Table II); and (2) the work of Bunker and co-workers [17,18] gives some justification for following this procedure. Bunker, McLarnon, and Moss [18] solve Eq. (1) with an effective vibrational mass $\mu_v = \mu(1+\beta)$, where

$$\beta = -\frac{2}{\mu}\sum_n |\langle 0|P_R|n\rangle|^2/\Delta_{0n} \ .$$

Here P_R is the momentum operator, $|0\rangle$ and $|n\rangle$ represent the ground and excited electronic states, respectively, and Δ_{0n} is the energy difference between states 0 and n. In general, β is an R-dependent function representing the nonadiabatic effect of distant electronic

states, but Bunker, McLarnon, and Moss [18] fit the eigenvalues of D_2 by assuming that β was a constant. They found that μ_v was much closer to the value calculated from atomic masses than from bare nuclear masses. However, Wolniewicz [6] comments that the procedure of calculating the eigenvalues from the bare masses and adding the calculated corrections due to the R-dependent nonadiabatic interactions gives much better agreement between the calculated and experimental vibrational quanta than does the semiempirical nonadiabatic result obtained by Bunker, McLarnon, and Moss [18].

We address the question of the effect of the R-dependent nonadiabatic (NA) corrections in a scattering calculation and show that the effect of these interactions can be included to a good approximation by a local effective-potential operator. Following Refs. [1–7] we solve Eq. (1) using the bare mass μ, but add a term $V_{NA}(R)$ to $V_{ABO}(R)$ to represent the effect of the interaction with distant electronic states. We use this method to calculate the eigenvalues and scattering lengths of the ground $X\,^1\Sigma_g^+$ state of H_2 and D_2. We also repeat the multichannel close-coupling calculations for ground-state collision-rate coefficients of $H+H$ and $D+D$ collisions, replacing the ground-state potential in Eq. (1) by the same effective potential, $V_{ABO}(R)+V_{NA}(R)$.

We first describe and parametrize the local nonadiabatic operator, and then calculate the scattering lengths and $J=0$ vibrational eigenvalues of H_2 and D_2. Finally, we briefly review the theory and calculations of spin relaxation rates for H_2 and its isotopic analogs.

II. THEORY

Wolniewicz [6] calculated the nonadiabatic interaction for the $X\,^1\Sigma_g^+$ state due to distant states of $^1\Sigma_g^+$ and $^1\Pi_g$ symmetry (ungerade states also contribute to mixed isotope states, such as HD). Only the $^1\Sigma_g^+$ states contribute to the shift of $J=0$ eigenvalues in H_2 and D_2, causing eigenvalue shifts of up to 5 cm^{-1} in H_2. However, the nonadiabatic corrections given by Wolniewicz and used by Schwartz and LeRoy [7] are vibrational averages for each specific level and are thus inapplicable to the continuum. Thus, we decided to develop an effective local operator to approximate the second-order nonadiabatic interactions. It is reasonable to expect that this R-dependent interaction is dominated by the rapid variation of the electronic wave function near the avoided crossing that gives rise to the double minimum feature in the $E,F\,^1\Sigma_g^+$ state. Therefore, we began with an initial Gaussian trial function that mimics the shape of the maximum in the $E,F\,^1\Sigma_g^+$ state and adjusted the amplitude to obtain a good fit to the $J=0$ eigenvalues of H_2. The trial function was then generalized to obtain further improvements in those eigenvalues. Figure 1 shows a plot of the $X\,^1\Sigma_g^+$ and the $E,F\,^1\Sigma_g^+$ $V_{ABO}(R)$ potentials along with the determined effective local operator. Table I tabulates the function we use, which was fit as a cubic spline and exponentially extrapolated outside its tabulated range. Table II shows the calculated differences Δ in the $J=0$ eigenvalues of H_2 relative to those calculated by Schwartz and LeRoy [7] for three different calculations. The calcu-
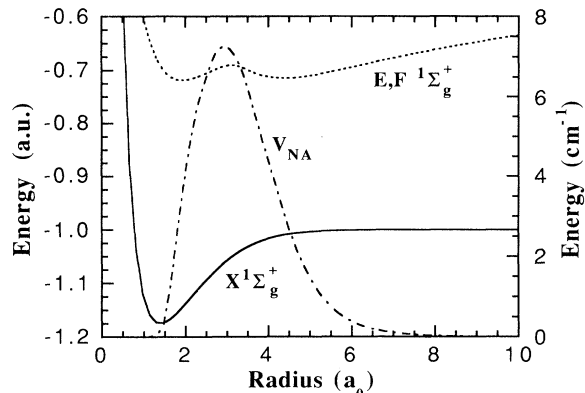

FIG. 1. Figure of the $X\,^1\Sigma_g^+$ (solid line) and $E,F\,^1\Sigma_g^+$ (short-dashed line) double minimum state, where the abscissa is given in units of the bohr radii $a_0=0.529\,177\,249\,0\times10^{-10}$ m. The asymmetric effective local operator V_{NA} (dash-dotted line), which describes the off-diagonal nonadiabatic interactions, is shown relative to the right-hand energy scale. Note that V_{NA} has its maximum near the hump in the $E,F\,^1\Sigma_g^+$ state.

lation labeled "bare" uses $\mu=m_p/2$ with $V_{ABO}(R)$ only; the one labeled "atomic" uses $\mu=m_H/2$ with $V_{ABO}(R)$ only; and the one labeled NA uses $\mu=m_p/2$ with $V_{ABO}(R)+V_{NA}(R)$. Here m_p and m_H are the respective proton and hydrogen atom masses. One should note that the calculation using the atomic mass provides a very good approximation to the full nonadiabatic calculation for the last vibrational eigenstate. All masses and conversion factors are consistent with the 1986 recommended values [19,20]. In order to check the accuracy of our effective local operator we performed a similar set of eigenvalue calculations for D_2, which use the corresponding masses for D. These are given in Table III. The effective local operator used for the D_2 calculations is identical to that used for the H_2 calculations, but has been scaled by the mass of the deuteron relative to the

TABLE I. Effective local operator $V_{NA}(R)$ used in our calculations.

Radius (units of a_0)	$V_{NA}d$ (cm^{-1})
1.565	−0.703 50
1.730	−1.978 64
1.880	−3.217 10
2.050	−4.404 30
2.225	−5.474 59
2.460	−6.344 71
2.650	−6.930 34
2.830	−7.233 60
3.050	−7.220 30
3.270	−6.911 86
3.520	−6.165 50
3.810	−5.079 47
4.090	−4.106 48
4.470	−2.797 84
5.055	−1.382 30
5.502	−0.762 13
5.950	−0.420 20
6.397	−0.231 67

TABLE II. Differences between the calculated H_2 eigenvalues and the eigenvalues obtained by Schwartz and LeRoy (Ref. [7]). In column 1 are the results of Schwartz and LeRoy; columns 2 through 4 are the current calculations using the bare nuclear mass and $V_{ABO}(R)+V_{NA}(R)$, the atomic mass and $V_{ABO}(R)$, and the bare nuclear mass and $V_{ABO}(R)$, respectively.

Quantum number	Calculated eigenvalues (cm^{-1})[a]	Δ_{NA} (cm^{-1})	Δ_{atomic} (cm^{-1})	Δ_{bare} (cm^{-1})
0	−36 118.074	−0.003	−0.086	0.502
1	−31 956.927	−0.003	−0.292	1.363
2	−28 031.088	−0.001	−0.482	2.115
3	−24 335.689	0.015	−0.607	2.809
4	−20 867.698	0.009	−0.722	3.391
5	−17 626.119	−0.009	−0.804	3.883
6	−14 612.257	−0.001	−0.768	4.364
7	−11 830.105	0.006	−0.704	4.738
8	−9286.901	0.000	−0.623	4.979
9	−6993.907	0.005	−0.511	5.082
10	−4967.499	0.009	−0.410	4.982
11	−3230.727	0.008	−0.299	4.653
12	−1815.600	−0.004	−0.188	4.033
13	−766.456	0.008	−0.105	3.007
14	−144.606	0.001	−0.051	1.457

[a]Reference [7].

mass of the proton. The largest difference in our nonadiabatic calculation for H_2 and D_2 eigenvalues, relative to those calculated by Schwartz and LeRoy, are, respectively, 0.015 and 0.031 cm^{-1}, as compared with an estimated uncertainty of 0.015 cm^{-1} in the eigenvalues of Schwartz and LeRoy. Therefore, the effective local operator is a good approximation for including nonadiabatic correc-

TABLE III. Same as Table II except for D_2.

Quantum number	Calculated eigenvalues (cm^{-1})[a]	Δ_{NA} (cm^{-1})	Δ_{atomic} (cm^{-1})	Δ_{bare} (cm^{-1})
0	−36 748.349	−0.005	−0.020	0.189
1	−33 754.742	0.006	−0.094	0.506
2	−30 880.242	0.012	−0.161	0.799
3	−28 122.759	0.023	−0.213	1.075
4	−25 480.643	0.002	−0.289	1.296
5	−22 952.701	0.005	−0.329	1.523
6	−20 538.231	0.031	−0.343	1.745
7	−18 237.066	0.029	−0.365	1.928
8	−16 049.615	−0.003	−0.395	2.072
9	−13 976.943	0.008	−0.370	2.237
10	−12 020.847	0.028	−0.329	2.384
11	−10 183.972	0.028	−0.300	2.482
12	−8469.946	0.020	−0.272	2.540
13	−6883.561	−0.009	−0.264	2.532
14	−5430.997	0.002	−0.220	2.511
15	−4120.111	0.017	−0.168	2.444
16	−2960.825	−0.004	−0.144	2.282
17	−1965.632	0.005	−0.092	2.073
18	−1150.258	0.004	−0.065	1.747
19	−534.551	0.013	−0.033	1.315
20	−143.336	0.009	−0.018	0.735
21	−1.648	0.000	−0.003	0.061

[a]Reference [7].

tions in the eigenvalue calculation. On the other hand, using the atomic mass to approximate the nonadiabatic corrections give significantly poorer eigenvalues, as previously reported by Wolniewicz [6].

We have calculated the scattering length A_1 on the $X\,^1\Sigma_g^+$ potential for various choices of the reduced mass and the effective local operator. These are given in Table IV, along with the scattering length A_3 for the $^3\Sigma_u$ state. The $X\,^1\Sigma_g^+$ scattering lengths for H+H and D+D collisions differ by about $0.15a_0$ between the bare mass and NA calculations. The percentage error is much larger for H+H because of the much smaller magnitude of the scattering length. Our scattering length for H+H collisions calculated using the bare masses and $V_{ABO}+V_{NA}$ agrees well with that calculated using the atomic mass and V_{ABO} only. It also agrees well with the scattering length of $A_1=0.32a_0$ reported by Stoof, Koelman, and Verhaar [16], and calculated from the earlier V_{ABO} potentials of Refs. [6,9,21,22]. This indicates that the choice of using the atomic masses without any explicit treatment of the R-dependent nonadiabatic corrections seems justified for scattering calculations.

We have also calculated the scattering length A_3 for the ground $^3\Sigma_u$ potential, using the two choices of masses, but without any nonadiabatic corrections, which are not known for this state. The two values from the bare mass and atomic mass calculations agree well with one another and with the value $A_3=1.34a_0$ reported by Stoof, Koelman, and Vehaar [16]. This implies the absence of significant nonadiabatic effects for this state.

In order to judge the role of R-dependent nonadiabatic effects on ground-state spin relaxation rates, we have also carried out full quantum scattering close-coupling calculations of these rates for H+H and D+D collisions using methods that are equivalent to those described by Stoof, Koelman, and Verhaar [16]. Three different sets of calculations were done in the limit of zero magnetic field using the assumptions of the bare mass, atomic mass, and NA calculations described above. In the NA calculation, V_{ABO} for the $X\,^1\Sigma_g^+$ state was replaced by $V_{ABO}+V_{NA}$. The full close-coupling equations were set up in a nuclear g/u symmetrized basis $|FMf_af_bl\rangle$, where $\mathbf{F}=\mathbf{S}_a+\mathbf{S}_b+\mathbf{I}_a+\mathbf{I}_b+\mathbf{l}$. $\mathbf{S}_k$ and $\mathbf{I}_k$ are the respective spin and nuclear angular momenta of atom $k=a,b$, $\mathbf{l}$ is the relative angular momentum of nuclear motion, and $\mathbf{F}$ is the total angular momentum. The S matrix obtained in this basis is then transformed by a unitary transformation

TABLE IV. Calculated scattering lengths (in units of a_0) for the bare nuclear mass and $V_{ABO}(R)$, respectively. There are no estimates for nonadiabatic interactions for the $b\,^3\Sigma_u^+$ state.

System[a]	Scattering length (units of a_0)		
	NA	Atomic	Bare
$H_2(X\,^1\Sigma_g^+)$	0.3159	0.3045	0.4539
$D_2(X\,^1\Sigma_g^+)$	12.97	12.97	13.11
$H_2(b\,^3\Sigma_u^+)$		1.340	1.343
$D_2(b\,^3\Sigma_u^+)$		−6.867	−6.858

[a]Reference [7].

to the $|f_a m_a f_b m_b l \mu \rangle$ basis, and the event rates calculated for the specific processes, $f_a m_a f_b m_b \rightarrow f'_a m'_a f'_b m'_b$.

There are two mechanisms for these hyperfine changing collisions, a spin-dipole and a spin-exchange process. The spin-dipole mechanism depends on the spin-spin interaction, which splits the degeneracy of the $\Omega = 0$ and 1 components of the $^3\Sigma_u$ state, where Ω is the projection of spin on the internuclear axis. Since this mechanism depends on the $^3\Sigma_u$ potential, we calculate nearly identical rate coefficients for spin-dipolar processes using bare mass, atomic mass, and NA calculations. These agree well with the graphical results for H+H [16] and D+D [14,15].

On the other hand, the spin-exchange mechanism depends on the phase differences between scattering on the $^3\Sigma_u$ and $X\,^1\Sigma_g^+$ states. In particular, Stoof, Koelman, and Verhaar [16] show that within the framework of their DIS approximation the rate coefficients for spin-exchange processes for H+H that go by s-wave collisions in the $T \rightarrow 0$ limit are proportional to $(A_1 - A_3)^2$. This difference is very sensitive to the nonadiabatic corrections in the H+H case. In fact, we find that exchange processes calculated for H+H by the bare method to be about 30% lower than those calculated by the NA method. However, spin-exchange rates calculated by the atomic mass and NA methods agree well with one another, and

also agree well with the previous calculations for H+H [16] and D+D [14,15].

On the basis of these calculations, we believe that the approximation of the "atomic" calculation, in which the atomic masses are used with the V_{ABO} potentials, are adequate to represent the low-temperature collision-rate coefficient for ground-state collisions, even though this approximation neglects the R dependence of the nonadiabatic corrections. We do wish to comment that this method is expected to locate incorrectly the position of shape resonances since the eigenvalues are not accurately calculated. This could affect the cross section at higher temperatures or in a strong magnetic field, where shape resonance effects may be important [23]. An alternate procedure to the one we use would be to develop an effective local operator which corrects the constant-atomic-mass approximation. In this way, the theory would have the correct asymptotic scattering properties and would also locate the eigenvalues more accurately.

ACKNOWLEDGMENTS

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