PHYSICAL REVIEW A **78**, 052503 (2008)

Electric dipole rovibrational transitions in the HD molecule

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(Received 20 August 2008; revised manuscript received 22 September 2008; published 7 November 2008)

The rovibrational electric dipole transitions in the ground electronic state of the HD molecule are studied. A simple, yet rigorous formula is derived for the transition rates in terms of the electric dipole moment function $D(R)$, which is calculated in a wide range of R. Our numerical results for transition rates are in moderate agreement with experiments and previous calculations, but are at least an order of magnitude more accurate.

DOI: 10.1103/PhysRevA.78.052503 PACS number(s): 33.70.Ca, 95.30.Ky, 31.15.−p, 31.30.−i

I. INTRODUCTION

The electric dipole rovibrational transitions in the HD molecule are possible due to different masses of the proton and of the deuteron and thus slightly different binding energies in hydrogen and deuterium. These transitions, for the first time, were observed by Herzberg [1] and since then measured by several groups [2–9]. Theoretical calculations of the dipole transition moment were first carried out by Wick [10], somewhat later by Wu [11], and by Blinder [12]. More elaborate calculations include those of Bunker [13], Wolniewicz [14], Ford and Browne [15], and Thorson *et al.* [16]. The most recent works [14–16] are in generally good agreement with experimental results in [3–9].

In this work we derive a compact formula for the dipole transition moment using a unitary transformation of the Hamiltonian followed by the adiabatic approximation, and present results in terms of the electric dipole moment function $D(R)$. We obtain $D(R)$ for a wide range of internuclear distances $R \in \langle 0.5, 12\rangle$ a.u., which enables calculations of electric dipole transitions between all rovibrational states including the highly excited ones. Although they have not been measured, these dipole transitions between highly excited states together with electric quadrupole transitions lead to the cooling of the hydrogen clouds in the interstellar space [17]. The obtained transition rates between low lying rovibrational states are the most accurate to date, and agree with experimental values with minor exceptions.

II. DERIVATION OF THE TRANSITION DIPOLE MOMENT

In order to derive a formula for the dipole transition moment, we consider a diatomic molecule in the reference frame of the geometrical center of the two nuclei. The total wave function ϕ is a solution of the stationary Schrödinger equation

$$H\phi = E\phi, \tag{1}$$

with the Hamiltonian

$$H = H_{\rm el} + H_{\rm n}, \tag{2}$$

split into the electronic and nuclear parts. In the electronic Hamiltonian

$$H_{\rm el} = -\sum_a \frac{\nabla_a^2}{2m_{\rm e}} + V, \tag{3}$$

with V including the Coulomb interaction, the nuclei have fixed positions $\vec{R}_A$ (proton) and $\vec{R}_B$ (deuteron), while the nuclear Hamiltonian is

$$H_{\rm n} = -\frac{\nabla_R^2}{2\mu_{\rm n}} - \frac{\left(\sum_a \vec{\nabla}_a\right)^2}{8\mu_{\rm n}} - \frac{1}{2}\left(\frac{1}{M_B} - \frac{1}{M_A}\right)\vec{\nabla}_R \cdot \sum_a \vec{\nabla}_a, \tag{4}$$

where $\vec{R}=\vec{R}_A-\vec{R}_B$ and $\mu_{\rm n}$ is the nuclear reduced mass. In the adiabatic approximation the total wave function of the molecule

$$\phi_{\rm a}(\vec{r},\vec{R}) = \phi_{\rm el}(\vec{r})_{\vec{R}}\,\chi(\vec{R}) \tag{5}$$

is represented as a product of the electronic wave function $\phi_{\rm el}$ and the nuclear wave function χ. The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

$$[H_{\rm el} - E_{\rm el}(R)]|\phi_{\rm el}\rangle = 0, \tag{6}$$

while the wave function χ is a solution to the nuclear Schrödinger equation with the effective potential generated by electrons

$$\left[-\frac{\nabla_R^2}{2\mu_{\rm n}} + \langle\phi_{\rm el}|H_{\rm n}|\phi_{\rm el}\rangle + E_{\rm el}(R) - E_{\rm a}\right]|\chi\rangle = 0, \tag{7}$$

where the so-called diagonal (or adiabatic) correction

$$\langle\phi_{\rm el}|H_{\rm n}|\phi_{\rm el}\rangle = \frac{1}{2\mu_{\rm n}}\langle\vec{\nabla}_R\phi_{\rm el}|\vec{\nabla}_R\phi_{\rm el}\rangle - \frac{1}{8\mu_{\rm n}}\langle\phi_{\rm el}|\left(\sum_a \vec{\nabla}_a\right)^2|\phi_{\rm el}\rangle \tag{8}$$

is a function of R.

The existence of the electric dipole transitions in HD is due to the last term in Eq. (4). This term can be used directly as a perturbation. Such an approach is presented in the Ap-

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1050-2947/2008/78(5)/052503(7)

pendix for a comparison with previous works. In an alternative method, inspired by the work of Thorson *et al.* [16] and applied here, we introduce a unitary transformation

$$H' = U^{+}HU \tag{9}$$

to shift the odd term in H_n to the potential V in Eq. (3). This transformation greatly simplifies further calculations. We choose U of the form

$$U = e^{\lambda(\vec{r}_1+\vec{r}_2)\cdot\vec{\nabla}_R}, \tag{10}$$

with

$$\lambda = -\frac{m_\mathrm{e}}{2}\left(\frac{1}{M_B}-\frac{1}{M_A}\right), \tag{11}$$

and obtain H' while neglecting $O(m_\mathrm{e}/\mu_\mathrm{n})^2$ terms, namely,

$$\begin{aligned} H' &= H + \lambda[H,(\vec{r}_1+\vec{r}_2)\cdot\vec{\nabla}_R] + O(\lambda^2) \\ &= H - \lambda(\vec{r}_1+\vec{r}_2)\cdot\vec{\nabla}_R(V) - \frac{\lambda}{m_\mathrm{e}}(\vec{\nabla}_1+\vec{\nabla}_2)\cdot\vec{\nabla}_R \\ &= H_\mathrm{el} + \delta V + H'_\mathrm{n}, \end{aligned} \tag{12}$$

where

$$\delta V = \frac{m_\mathrm{e}}{2}\left(\frac{1}{M_B}-\frac{1}{M_A}\right)(\vec{r}_1+\vec{r}_2)\cdot\vec{\nabla}_R(V), \tag{13}$$

$$\vec{\nabla}_R(V) = \frac{1}{2}\left(-\frac{\vec{r}_{1A}}{r_{1A}^3}+\frac{\vec{r}_{1B}}{r_{1B}^3}-\frac{\vec{r}_{2A}}{r_{2A}^3}+\frac{\vec{r}_{2B}}{r_{2B}^3}\right)-\frac{\vec{n}}{R^2}, \tag{14}$$

$$H'_\mathrm{n} = -\frac{\nabla_R^2}{2\mu_\mathrm{n}} - \frac{\left(\sum_a \vec{\nabla}_a\right)^2}{8\mu_\mathrm{n}}, \tag{15}$$

and $\vec{n}=\vec{R}/R$.

The **E**1 transition between rovibrational levels of the HD molecule in the ground electronic state comes now from the nonadiabatic correction δV to the electronic potential V. In the leading order one uses the adiabatic approximation, and the electric dipole moment $\vec{D}_\mathrm{fi}$ between some initial φ_i and final state φ_f is

$$\vec{D}_\mathrm{fi} = \langle\phi_\mathrm{f}|\vec{r}|\phi_\mathrm{i}\rangle \tag{16}$$

$$= \langle\phi_\mathrm{el}\chi_\mathrm{f}|\vec{r}\frac{1}{E_\mathrm{el}-H_\mathrm{el}}\delta V|\phi_\mathrm{el}\chi_\mathrm{i}\rangle + \langle\phi_\mathrm{el}\chi_\mathrm{f}|\delta V\frac{1}{E_\mathrm{el}-H_\mathrm{el}}\vec{r}|\phi_\mathrm{el}\chi_\mathrm{i}\rangle, \tag{17}$$

where $\vec{r}=\Sigma_a\vec{r}_a$. We claim, without presenting the proof, that the higher-order nonadiabatic corrections are smaller by a factor of $m_\mathrm{e}/\mu_\mathrm{n}\approx 10^{-3}$, and their contribution to $\vec{D}_\mathrm{fi}$ can be neglected.

Below, we rewrite this matrix element in terms of the electric dipole moment function $D(R)$, namely,

$$\vec{D}_\mathrm{fi} = \langle\chi_\mathrm{f}|D\vec{n}|\chi_\mathrm{i}\rangle = \langle J_\mathrm{f},M_\mathrm{f}|\vec{n}|J_\mathrm{i},M_\mathrm{i}\rangle D_\mathrm{fi}, \tag{18}$$

$$D_\mathrm{fi} = \int dR R^2 D(R)\chi^*_{J_\mathrm{f}}(R)\chi_{J_\mathrm{i}}(R), \tag{19}$$

$$D(R) \equiv \left(\frac{m_\mathrm{e}}{M_B}-\frac{m_\mathrm{e}}{M_A}\right)\langle\phi_\mathrm{el}|\vec{r}\cdot\vec{n}\frac{1}{E_\mathrm{el}-H_\mathrm{el}}\vec{r}\cdot\vec{\nabla}_R(V)|\phi_\mathrm{el}\rangle. \tag{20}$$

The function $D(R)$ depends only on the distance R between the nuclei. Although similar, $D(R)$ cannot be identified with the projection of the dipole moment operator onto the symmetry axis, because the direction of $\vec{R}$ is changed under applied unitary transformation.

III. NUMERICAL CALCULATIONS

For the numerical calculation of $D(R)$, the clamped nuclei electronic wave functions were represented in the form of linear expansions in the two-electron basis of exponentially correlated Gaussian (ECG) functions

$$\psi_k(\vec{r}_1,\vec{r}_2) = \frac{1}{4}(1+\hat{P}_{12})(1\pm\hat{\imath}) \times\exp\left[-\sum_{i,j=1}^{2}A_{k,ij}(\vec{r}_i-\vec{s}_{k,i})(\vec{r}_j-\vec{s}_{k,j})\right], \tag{21}$$

where the matrices $\mathbf{A}_k$ and vectors $\vec{s}_k$ contain nonlinear parameters, five per basis function, to be variationally optimized. The Gaussian centers $\vec{s}_k$ were constrained to the internuclear axis to preserve the Σ symmetry. The antisymmetry projector $(1+\hat{P}_{12})$ ensures singlet symmetry and the spatial projector $(1\pm\hat{\imath})$—the gerade (+) or ungerade (−) symmetry with respect to inversion in the origin of the coordinate system located at the geometric center of the nuclei.

The computations were performed independently at 56 internuclear distances. In order to check the asymptotic behavior of the dipole moment function, long distances (up to $R=12.0$ a.u.) were sampled. At every distance R, two 600-term basis sets were generated—one, of the ${}^1\Sigma_g^+$ symmetry, to represent the electronic ground state wave function ϕ_el, and the other, of the ${}^1\Sigma_u^+$ symmetry, to invert the Hamiltonian. The parameters of the first basis set were optimized with respect to the lowest root of the clamped nuclei Hamiltonian H_el and the electronic energy was converged to an accuracy of the order of a fraction of microhartree. The nonlinear parameters of the second basis were optimized with respect to the functional corresponding to the parallel polarizability

$$\mathcal{J} = \langle\phi_\mathrm{el}|\vec{r}\cdot\vec{n}\frac{1}{H_\mathrm{el}-E_\mathrm{el}}\vec{r}\cdot\vec{n}|\phi_\mathrm{el}\rangle, \tag{22}$$

with the fixed ϕ_el wave function. The basis sets generated this way were subsequently employed to evaluate the dipole moment $D(R)$, Eq. (20). The proton and the deuteron mass used in Eq. (20) were taken from [19]

$$M_A \equiv M_\mathrm{H} = 1836.152\,672\,47\, m_\mathrm{e}, \tag{23}$$

TABLE I. $D(R)$—the electric dipole moment (in 10^{-4} D) as a function of the internuclear distance R. All digits are numerically significant.

$R/(\text{a.u.})$	$D(R)$	$R/(\text{a.u.})$	$D(R)$
0.5	−27.6224	3.2	−5.0893
0.6	−21.0635	3.3	−4.7735
0.7	−17.0294	3.4	−4.4482
0.8	−14.3747	3.5	−4.1182
0.9	−12.5426	3.6	−3.7882
1.0	−11.2339	3.8	−3.1468
1.1	−10.2754	4.0	−2.5552
1.2	−9.5603	4.2	−2.0342
1.3	−9.0193	4.4	−1.5928
1.4	−8.6054	4.5	−1.4022
1.45	−8.4353	4.6	−1.2307
1.5	−8.2853	4.8	−0.9409
1.6	−8.0347	5.0	−0.7137
1.7	−7.8352	5.2	−0.5381
1.8	−7.6721	5.25	−0.5010
1.9	−7.5336	5.5	−0.3495
2.0	−7.4102	5.75	−0.2428
2.1	−7.2933	6.0	−0.1682
2.2	−7.1758	6.5	−0.0804
2.3	−7.0517	7.0	−0.0384
2.4	−6.9156	7.5	−0.0184
2.5	−6.7632	8.0	−0.0089
2.6	−6.5913	8.5	−0.0044
2.7	−6.3972	9.0	−0.0022
2.8	−6.1799	9.5	−0.0012
2.9	−5.9390	10.0	−0.0006
3.0	−5.6755	11.0	−0.0002
3.1	−5.3911	12.0	−0.0001

$$M_B \equiv M_{\text{D}} = 3670.482\,965\,4\; m_{\text{e}}. \qquad (24)$$

The dipole moment is commonly expressed in units of debye (D), and the numerical factor used in this work to convert the results from the atomic to debye units was 2.541 746 23 D/a.u. To inspect the saturation of the $^1\Sigma_u^+$ basis at $R=1.4$ a.u., we generated an additional 600-term basis set with the nonlinear parameters optimized with respect to

$$\langle \phi_{\text{el}} | \vec{r} \cdot \vec{\nabla}_R(V) \frac{1}{H_{\text{el}} - E_{\text{el}}} \vec{r} \cdot \vec{\nabla}_R(V) | \phi_{\text{el}} \rangle, \qquad (25)$$

and combined this basis set with the original $^1\Sigma_u^+$ basis. Despite doubling the size of the basis set, the $D(R)$ value has changed only on the eighth significant figure. Hence, we expect that all displayed figures of the final result in Table I are significant.

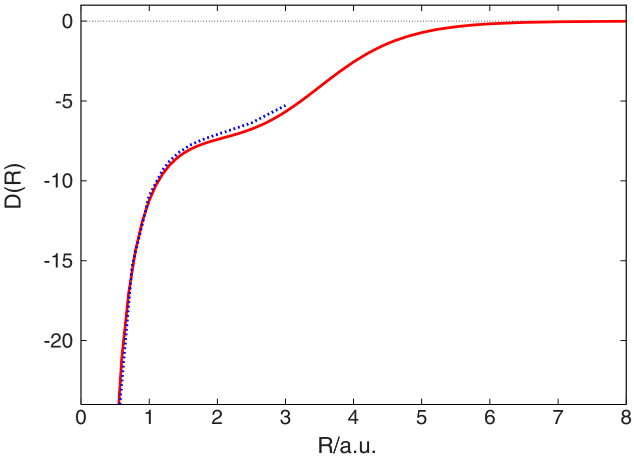

FIG. 1. (Color online) Electric dipole moment function $D(R)$ (in 10^{-4} D). A comparison to previous calculations by Ford and Browne [15] (dotted line). $\vec{n}$ is directed from deuteron to proton. Negative $D(R)$ means that electrons are shifted toward the deuteron.

Numerical values of the $D(R)$ function are presented in Table I and plotted in Fig. 1. For comparison with previous calculations, the dipole moment function obtained by Ford and Browne [15] in the range of $R \in \langle 0.5, 3.0 \rangle$ a.u. is presented in the same Fig. 1. The function $D(R)$ behaves as R^{-2} at $R \to 0$, and as R^{-4} at $R \to \infty$. The singularity at $R=0$ comes from neglecting higher-order terms in the unitary transformation and from the adiabatic approximation. At R of the order $\sqrt{m_{\text{e}}/\mu_{\text{n}}} \approx 0.03$ adiabatic approximation fails and our formula for $D(R)$ is not valid. At this region, however, the nuclear wave function is negligible.

For the calculation of the electric dipole moments, the adiabatic potential of the nuclear Schrödinger equation (7) has been composed of the clamped nuclei energy E_{el}, and the adiabatic correction $\langle \phi_{\text{el}} | H_{\text{n}} | \phi_{\text{el}} \rangle$. For E_{el} we used the energy points computed with nanohartree accuracy by Cencek from 1200-term ECG wave functions [20]. The adiabatic correction in Eq. (8) was evaluated by us using Eq. (A15). The adiabatic potential curve was then obtained by means of piecewise polynomial interpolation. The radial Schrödinger equation has been solved numerically using the Le Roy code [21]. The obtained nuclear wave functions χ of rovibrational levels were subsequently used in the evaluation of the dipole transition moments of Eq. (18) for the $J \to J+1$ transitions (branch R) and for the $J \to J-1$ transitions (branch P).

IV. RESULTS AND DISCUSSION

Our electric dipole moments for the transitions between the lowest vibrational and rotational levels are listed in Table II. Except for 0-0 transitions, they are in good agreement with the previous calculation by Thorson *et al.* For the lowest band all theoretical predictions differ slightly from each other. Our results are numerically accurate to all digits shown, but the last digit is uncertain due to the neglected $O(m_{\text{e}}/\mu_{\text{n}}) \approx 8 \times 10^{-4}$ higher-order nonadiabatic corrections. These corrections have also been neglected in calculations of [15,16], so, in principle, these calculations should agree with each other. Considering calculations presented in [14], we note that in the initial expression for $\vec{D}_{\text{fi}}$, Wolniewicz uses H_{n}'', Eq. (A1), as a perturbation, and assumes the adiabatic approximation for the wave function, but in the denominator

TABLE II. Experimental and theoretical electric dipole transition moments D_{fi} (in 10^{-4} D). Relative uncertainty of our results due to the nonadiabatic corrections to D_{fi} is about 10^{-3}.

Reference	$P(3)$	$P(2)$	$P(1)$	$R(0)$	$R(1)$	$R(2)$	$R(3)$
0-0							
Experiment [3]					9.36(30)	8.00(20)	9.79(30)
Experiment [4]					8.78(2)	8.47(2)	10.21(2)
Theory [14]				8.36	8.38	8.39	8.41
Theory [15]	8.282	8.297	8.306	8.306	8.297	8.282	8.262
Theory [16]	8.440	8.455	8.463	8.463	8.455	8.440	8.420
This work	8.536	8.551	8.560	8.560	8.551	8.536	8.516
1-0							
Experiment [6]	0.330(40)	0.405(30)	0.450(30)	0.515(20)	0.550(30)	0.615(30)	0.655(40)
Experiment [7]	0.340(22)	0.379(12)	0.435(11)	0.504(12)	0.533(14)		0.609(13)
Theory [14]				0.598	0.628	0.656	0.685
Theory [15]	0.401	0.445	0.485	0.560	0.594	0.623	0.650
Theory [16]	0.374	0.421	0.466	0.552	0.592	0.630	0.665
This work	0.3776	0.4248	0.4708	0.5579	0.5983	0.6362	0.6714
2-0							
Experiment [6]			0.17(2)	0.19(2)	0.20(2)		
Theory [14]				0.160	0.166	0.170	0.174
Theory [15]	0.156	0.167	0.176	0.192	0.199	0.206	0.210
Theory [16]	0.156	0.167	0.179	0.200	0.210	0.219	0.228
This work	0.1576	0.1692	0.1805	0.2022	0.2122	0.2216	0.2301
3-0							
Experiment [6]				0.0795(35)	0.0800(50)		
Theory [14]				0.100	0.102	0.103	0.104
Theory [15]	0.068	0.072	0.076	0.082	0.084	0.085	0.087
Theory [16]	0.0698	0.0742	0.0786	0.0870	0.0909	0.0945	0.0979
This work	0.0705	0.0749	0.0794	0.0878	0.0918	0.0955	0.0989
4-0							
Experiment [8]			0.0397(26)	0.0417(24)	0.0425(21)	0.0459(26)	0.0514(53)
Theory [14]				0.056	0.056	0.055	0.053
Theory [15]	0.033	0.035	0.038	0.039	0.040	0.042	0.042
Theory [16]	0.0324	0.0345	0.0365	0.0405	0.0425	0.0442	0.0458
This work	0.0327	0.0348	0.0369	0.0409	0.0428	0.0446	0.0462
5-0							
Experiment [9]	0.0105(25)	0.0124(21)	0.0143(17)	0.0181(17)	0.0200(21)	0.0219(25)	0.0238(29)
Experiment [8]				0.0207(20)	0.0214(14)	0.0231(21)	
Theory [15]	0.020	0.021	0.021	0.023	0.023	0.024	0.024
Theory [16]	0.0163	0.0173	0.0184	0.0205	0.0215	0.0225	0.0233
This work	0.0164	0.0175	0.0186	0.0207	0.0217	0.0227	0.0235

he includes H_{n}' from Eq. (15). This expression, in comparison to ours, involves some higher-order terms, namely, X_1 of Eq. (A12) from the Appendix. However, we show in the Appendix the cancellation of significant contributions involving the second derivative of χ between X_1 and the other-higher order contributions X_2 [Eq. (A13)] and X_3 [Eq. (A14)], which have been neglected in Wolniewicz calculations by assuming the adiabatic wave function. Therefore, we think, a slight difference with the results of Wolniewicz in [14] may come from less consistent treatment of higher-order nonadiabatic effects.

In comparison to experimental values, we observe a moderate agreement for all transitions but the 0-0 ones. Here, our results, as well as the other theoretical calculations, differ from the experiment by several standard deviations. We note, however, that the measurements are most cumbersome for these transitions. As a consequence, experimental values significantly change with the rotational number J for $v=0$, which cannot be justified by theoretical analysis. Within the ground vibronic state, the nuclear wave functions corresponding to the lowest rotational levels are localized near the average internuclear distance R_0, and differ very little from each other. For this reason subsequent transition moments must change slowly with the rotational quantum number J, and are approximately equal to $D(R_0)$, but the experimental results of [3,4] are not consistent with theoretical predictions.

V. CONCLUSIONS

We have derived a simple expression for the electric dipole transition rates, in terms of the dipole moment function $D(R)$, and performed precise calculations of $D(R)$ in a wide range of R. The obtained formula can easily be extended to other diatomic molecules, consisting of two isotopes of the same element. Our results for the dipole moments of the HD molecule are numerically accurate to four digits, in moderate agreement with previous calculations in [14–16] and experimental results of [3–9] (see Table II). We estimate that the relativistic and nonadiabatic corrections are of relative order of 10^{-4} and 10^{-3}, correspondingly. As no other effect may alter the theoretical predictions, we suppose that our results are more accurate than the experimental values obtained so far.

ACKNOWLEDGMENT

We are indebted to L. Wolniewicz for valuable comments.

APPENDIX

For a comparison with previous works [14,15], which used the term

$$H_{\rm n}'' = -\frac{1}{2}\left(\frac{1}{M_B} - \frac{1}{M_A}\right)\vec{\nabla}_R \cdot \sum_a \vec{\nabla}_a \tag{A1}$$

as a perturbation, we derive the formula for $\vec{D}_{\rm fi}$, Eq. (17), using the nonadiabatic perturbation theory. For this, one has to abandon the assumption in Eq. (5) of a separation of the electronic wave function from the nuclear one. Namely, the total wave function

$$\phi = \phi_{\rm a} + \delta\phi_{\rm na} = \phi_{\rm el}\chi + \delta\phi_{\rm na} \tag{A2}$$

will be the sum of the adiabatic solution and a nonadiabatic correction. The nonadiabatic correction $\delta\phi_{\rm na}$ is decomposed into two parts,

$$\delta\phi_{\rm na} = \phi_{\rm el}\delta\chi + \delta'\phi_{\rm na}, \tag{A3}$$

which obey the following orthogonality conditions:

$$\langle\delta'\phi_{\rm na}|\phi_{\rm el}\rangle_{\rm el} = 0, \tag{A4}$$

$$\langle\delta\chi|\chi\rangle = 0, \tag{A5}$$

with the normalization $\langle\phi|\phi_a\rangle=1$. In the leading order of perturbative treatment, the nonadiabatic corrections to the wave function are the following [18]:

$$|\delta'\phi_{\rm na}^{(1)}\rangle = \frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}|\phi_{\rm el}\chi\rangle, \tag{A6}$$

$$|\delta\chi\rangle = \frac{1}{[E_{\rm a}-E_{\rm el}-H_{\rm n}-\langle H_{\rm n}\rangle_{\rm el}]'}\langle\phi_{\rm el}|H_{\rm n}|\delta'\phi_{\rm na}\rangle_{\rm el}, \tag{A7}$$

where the prime in the denominator denotes subtraction of the reference state from the Hamiltonian inversion. For the calculation of $D(R)$ one needs also the second-order correction

$$\begin{aligned}|\delta'\phi_{\rm na}^{(2)}\rangle = {}& \frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}|\phi_{\rm el}(\chi+\delta\chi)\rangle + \frac{1}{(E_{\rm el}-H_{\rm el})'}\\ &\times[H_{\rm n}+E_{\rm el}-E_{\rm a}]\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}|\phi_{\rm el}\chi\rangle,\end{aligned} \tag{A8}$$

where $\delta\chi$ is given by Eq. (A7).

The derivation of the formula (20) proceeds as follows. One takes Eq. (16) with perturbed wave functions,

$$\begin{aligned}\vec{D}_{\rm fi} &= \langle\phi_{\rm el}(\chi_{\rm f}+\delta\chi_{\rm f}) + \delta'\phi_{\rm f,na}|\vec{r}|\phi_{\rm el}(\chi_{\rm i}+\delta\chi_{\rm i}) + \delta'\phi_{\rm i,na}\rangle,\\ &= \vec{D}_{\rm fi}^{(1)} + \vec{D}_{\rm fi}^{(2)},\end{aligned} \tag{A9}$$

$$\vec{D}_{\rm fi}^{(1)} = \langle\phi_{\rm el}\chi_{\rm f}|\vec{r}\frac{1}{E_{\rm el}-H_{\rm el}}H_{\rm n}''|\phi_{\rm el}\chi_{\rm i}\rangle + \langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}''\frac{1}{E_{\rm el}-H_{\rm el}}\vec{r}|\phi_{\rm el}\chi_{\rm i}\rangle, \tag{A10}$$

and $\vec{D}_{\rm fi}^{(2)}$ is given in Eq. (A19). In the $\vec{D}_{\rm fi}^{(1)}$ one separates out the electronic matrix elements from the nuclear ones, namely,

$$\begin{aligned}D_{\rm fi}^{(1)k} = {}& -\frac{1}{2}\left(\frac{1}{M_B}-\frac{1}{M_A}\right)\int d^3R\biggl\{\chi_{\rm f}^\star\chi_{\rm i}\,2\langle\phi_{\rm el}|r^k\\ &\times\frac{1}{E_{\rm el}-H_{\rm el}}\vec{\nabla}_R\cdot\sum_a\vec{\nabla}_a|\phi_{\rm el}\rangle + (\chi_{\rm f}^\star\nabla_R^j\chi_{\rm i} + \chi_{\rm i}\nabla_R^j\chi_{\rm f}^\star)\\ &\times\langle\phi_{\rm el}|r^k\frac{1}{E_{\rm el}-H_{\rm el}}\sum_a\vec{\nabla}_a^j|\phi_{\rm el}\rangle\biggr\},\end{aligned} \tag{A11}$$

where the superscripts j and k are the Cartesian indices. The second term in braces is integrated by parts and $D_{\rm fi}^{(1)k}$ becomes

$$\begin{aligned}D_{\rm fi}^{(1)k} = {}& -\frac{1}{2}\left(\frac{1}{M_B}-\frac{1}{M_A}\right)\int d^3R\chi_{\rm f}^\star\chi_{\rm i}\\ &\times[\langle\phi_1^k|\nabla_R^j\phi_2^j\rangle - \langle\nabla_R^j\phi_1^k|\phi_2^j\rangle],\end{aligned} \tag{A12}$$

where

$$|\phi_1^k\rangle = \frac{1}{E_{\rm el}-H_{\rm el}}r^k|\phi_{\rm el}\rangle, \tag{A13}$$

$$|\phi_2^j\rangle = \sum_a\nabla_a^j|\phi_{\rm el}\rangle = -(H_{\rm el}-E_{\rm el})m_{\rm e}r^j|\phi_{\rm el}\rangle. \tag{A14}$$

One takes $\vec{\nabla}_R$ of the Schrödinger equation (6) to obtain

$$\nabla_R^j \phi_{\rm el} = \frac{1}{(E_{\rm el}-H_{\rm el})'}\nabla_R^j(V)\phi_{\rm el}, \tag{A15}$$

$$\nabla_R^j \phi_1^k = \frac{1}{E_{\rm el}-H_{\rm el}}\biggl[\nabla_R^j(V-E_{\rm el})\frac{1}{E_{\rm el}-H_{\rm el}}r^k\phi_{\rm el} + r^k\frac{1}{(E_{\rm el}-H_{\rm el})'}\nabla_R^j(V)\phi_{\rm el}\biggr], \tag{A16}$$

$$\nabla_R^j \phi_2^j = -\nabla_R^j(V-E_{\rm el})m_{\rm e}r^j\phi_{\rm el} + (E_{\rm el}-H_{\rm el})m_{\rm e}r^j\frac{1}{(E_{\rm el}-H_{\rm el})'}\nabla_R^j(V)\phi_{\rm el}. \tag{A17}$$

The gradient of the electronic functions with respect to the internuclear distance in Eq. (A12) is replaced by Eqs. (A16) and (A17). Among the four terms, two cancel out and the other two are the same, so the transition dipole moment takes the form

$$D_{\rm fi}^{(1)k} = \left(\frac{m_{\rm e}}{M_B}-\frac{m_{\rm e}}{M_A}\right)\int d^3R\,\chi_{\rm f}^\star\chi_{\rm i} \times \langle\phi_{\rm el}|r^k\frac{1}{E_{\rm el}-H_{\rm el}}\vec{r}\cdot\vec{\nabla}_R(V-E_{\rm el})|\phi_{\rm el}\rangle. \tag{A18}$$

One notes that it differs from Eq. (20) only by the presence of $\vec{\nabla}_R E_{\rm el}$. We show below that this term cancels out with $D_{\rm fi}^{(2)k}$ given by

$$\begin{aligned}\vec{D}_{\rm fi}^{(2)} ={}& \langle\phi_{\rm el}\chi_{\rm f}|\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})'}[H_{\rm n}+E_{\rm el}-E_{\rm i,a}] \times\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}|\phi_{\rm el}\chi_{\rm i}\rangle\\ &+\langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}\frac{1}{(E_{\rm el}-H_{\rm el})'}\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n} \times|\phi_{\rm el}\chi_{\rm i}\rangle+\langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}\frac{1}{(E_{\rm el}-H_{\rm el})'}\\ &\times[H_{\rm n}+E_{\rm el}-E_{\rm f,a}]\frac{1}{(E_{\rm el}-H_{\rm el})'}\vec{r}|\phi_{\rm el}\chi_{\rm i}\rangle,\end{aligned} \tag{A19}$$

where we neglected $\delta\chi$. For low lying rovibrational states $\delta\chi/\chi$ is small, namely, of $O(m_{\rm e}/\mu_{\rm n})$ and thus its magnitude is of order 10^{-3}, if not less, and thus negligible. $H_{\rm n}$ is decomposed into the even $H_{\rm n}'$ parts, Eq. (15), and the odd $H_{\rm n}''$ parts, Eq. (A1). $\vec{D}_{\rm fi}^{(2)}$ involves the terms with a single power of $H_{\rm n}'$. The resulting six terms in $\vec{D}_{\rm fi}^{(2)}$ we group into pairs as follows:

$$\vec{D}_{\rm fi}^{(2)} = \vec{X}_1+\vec{X}_2+\vec{X}_3, \tag{A20}$$

$$\begin{aligned}\vec{X}_1 ={}& \langle\phi_{\rm el}\chi_{\rm f}|\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})}[H_{\rm n}'+E_{\rm el}-E_{\rm i,a}] \times\frac{1}{(E_{\rm el}-H_{\rm el})}H_{\rm n}''|\phi_{\rm el}\chi_{\rm i}\rangle\\ &+\langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}''\frac{1}{(E_{\rm el}-H_{\rm el})} \times[H_{\rm n}'+E_{\rm el}-E_{\rm f,a}]\frac{1}{(E_{\rm el}-H_{\rm el})}\vec{r}|\phi_{\rm el}\chi_{\rm i}\rangle,\end{aligned} \tag{A21}$$

$$\begin{aligned}\vec{X}_2 ={}& \langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}'\frac{1}{(E_{\rm el}-H_{\rm el})'}\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})}H_{\rm n}''|\phi_{\rm el}\chi_{\rm i}\rangle\\ &+\langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}''\frac{1}{(E_{\rm el}-H_{\rm el})}\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}'|\phi_{\rm el}\chi_{\rm i}\rangle,\end{aligned} \tag{A22}$$

$$\begin{aligned}\vec{X}_3 ={}& \langle\phi_{\rm el}\chi_{\rm f}|\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})}H_{\rm n}''\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}'|\phi_{\rm el}\chi_{\rm i}\rangle\\ &+\langle\phi_{\rm el}\chi_{\rm f}|H_{\rm n}'\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}''\frac{1}{(E_{\rm el}-H_{\rm el})}\vec{r}|\phi_{\rm el}\chi_{\rm i}\rangle.\end{aligned} \tag{A23}$$

$H_{\rm n}'$ involves two derivatives over R, and $H_{\rm n}''$, a single derivative. Consider terms with three derivatives of χ. Since χ satisfies Eq. (7), the second derivative of χ coming from $H_{\rm n}'$ cancels with $E_{\rm a}-E_{\rm el}(R)$, leaving a small term $\langle H_{\rm n}'\rangle_{\rm el}$ and the derivative of $E_{\rm el}$. Thus no term with three derivatives of χ is present. We will show below that no terms involving any derivatives of χ are present. Each $\vec{X}_i$ includes two derivatives,

$$X_1^k \approx \frac{1}{2\mu_n}\left(\frac{1}{M_B}-\frac{1}{M_A}\right) \times\int d^3R[\chi_{\rm f}^*(\nabla_R^l\nabla_R^j\chi_{\rm i})+\chi_{\rm i}(\nabla_R^l\nabla_R^j\chi_{\rm f}^*)] \times\langle\phi_{\rm el}|r^k\frac{1}{E_{\rm el}-H_{\rm el}}r^j|\nabla_R^l\phi_{\rm el}\rangle, \tag{A24}$$

$$X_2^k \approx \frac{1}{2\mu_n}\left(\frac{1}{M_B}-\frac{1}{M_A}\right) \times\int d^3R[(\nabla_R^l\chi_{\rm f}^*)(\nabla_R^j\chi_{\rm i})+(\nabla_R^j\chi_{\rm f}^*)(\nabla_R^l\chi_{\rm i})] \times\langle\phi_{\rm el}|r^jr^k\frac{1}{E_{\rm el}-H_{\rm el}}|\nabla_R^l\phi_{\rm el}\rangle, \tag{A25}$$

$$X_3^k \approx -X_1^k - X_2^k, \tag{A26}$$

but all of them cancel out in the sum. A single derivative of χ has to be of the form $\vec{\nabla}_R(\chi_{\rm f}^*\chi_{\rm i})$, which can be integrated by parts and transformed into derivatives of $\phi_{\rm el}$ and the resolvent. Considering terms without derivatives of χ, all of them are of order $O[(m_{\rm e}/m_{\rm n})^2]$ but one, which involves $\vec{\nabla}_R E_{\rm el}$, which arose from the commutator $[H'_{\rm n}+E_{\rm el}(R)-E_{\rm a},\vec{\nabla}_R]$ in X_1 in Eq. (A21). It is of the form

$$\vec{D}^{(2)}_{\rm fi}=\left(\frac{m_{\rm e}}{M_B}-\frac{m_{\rm e}}{M_A}\right)\langle\phi_{\rm el}\chi_{\rm f}|\vec{r}\frac{1}{(E_{\rm el}-H_{\rm el})'}\vec{r}\cdot\vec{\nabla}_R(E_{\rm el})|\phi_{\rm el}\chi_{\rm i}\rangle, \tag{A27}$$

which together with $\vec{D}^{(1)}_{\rm fi}$ gives the leading correction to the transition dipole moment, Eq. (17).

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