Analog of the Hellmann-Feynman theorem in multichannel quantum-defect theory

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A multichannel quantum-defect theory (MQDT) is employed to obtain expressions for nonadiabatic coupling matrix elements without recourse to knowledge of the electronic wave functions. Diagonal and nondiagonal analogs of the Hellmann-Feynman theorem are derived by a differentiation of the MQDT quantization equations with respect to internuclear distance R. Closed relations for both the adiabatic correction terms and the nonadiabatic matrix elements are given in terms of nuclear derivatives of the reactance matrix. The theory is tested by calculating the adiabatic correction and nonadiabatic radial and angular coupling matrix elements for the $g,h\,{}^3\Sigma_g^+$ and $4s,4d\,{}^3\Sigma_g^+$ states, corresponding to the first members ($n=3$ and 4) of the $s,d\,{}^3\Sigma_g^+$ Rydberg complex of the H_2 molecule. The derived estimates agree well with available *ab initio* results.

I. INTRODUCTION

Traditional nonadiabatic coupling theory is based on the following familiar Hellmann-Feynman results: [1,2]

$$\partial E_\alpha^{BO} = \langle \Psi_\alpha^{BO} | \partial H^{el} | \Psi_\alpha^{BO} \rangle, \tag{1}$$

$$B_{\alpha\beta} = \langle \Psi_\alpha^{BO} | \partial \Psi_\beta^{BO} \rangle = \langle \Psi_\alpha^{BO} | \partial H^{el} | \Psi_\beta^{BO} \rangle / (E_\alpha^{BO} - E_\beta^{BO}), \tag{2}$$

where $E_\alpha^{BO}, \Psi_\alpha^{BO}$ are eigenvalues and eigenfunctions of the Born-Oppenheimer electronic Schrödinger equation and the symbol ∂ denotes the first partial derivative with respect to R. Difficulties arise however in applying these equations to real molecular systems because the accuracy of most conventional *ab initio* methods rapidly decreases as the principal quantum number increases. Moreover, the treatment of non-Born-Oppenheimer effects for highly excited molecular states [3] may involve the tedious calculation of nonadiabatic coupling matrix elements [4] between numerous electronic states.

The purpose of this paper is to develop a Hellmann-Feynman version of multichannel quantum-defect theory (MQDT) [5] to handle the nonadiabatic coupling problem for molecular Rydberg states without recourse to the nuclear dependence of electronic wave functions. The idea behind the molecular MQDT approach, which combines Seaton's quantum-defect theory [6] with Fano's frame transformation method [7], is to treat the interaction between Rydberg electrons and their positive-ion cores as a scattering problem, normally formulated in terms of an energy insensitive but nuclear coordinate dependent reactance matrix $\mathbf{K}(\mathbf{R})$, in terms of which the main adiabatic corrections and nonadiabatic effects are taken into account *in intrinsic form*, without the evaluation of the corresponding electronic matrix elements [8]. Determination of the matrix $\mathbf{K}(\mathbf{R})$ requires knowledge only of the *ab initio* BO potentials of a small number of low-lying electronic states [9]. While impressive applications of the full theory to the interpretation of molecular absorption and autoionization spectra are available in the literature [10–13], our limited aim is to build a largely analytical bridge between the full MQDT method and more traditional approaches to nonadiabatic coupling. It is an extension of a previous single-channel version of the theory [14], in which we showed how the nonadiabatic coupling matrix elements could be extracted from knowledge of the bond-length dependence of the approximately energy independent quantum-defect function $\mu(R)$, which determines an infinite series of Born-Oppenheimer curves converging onto the positive-ion potential $E_{core}^{BO}(R)$ according to the equation [8,15]

$$E_n^{BO}(R) = E_{core}^{BO}(R) - \frac{1}{2[n-\mu(R)]^2}. \tag{3}$$

Thus *ab initio* determination of $E_n^{BO}(R)$ for say $n=3$ determines $\mu(R)$ and hence all higher curves.

The present extension of this approach to multichannel (or multiconfiguration) situations requires knowledge of the scattering reactance matrix $\mathbf{K}(\mathbf{R})$, the diagonal terms of which play roughly the same role as the quantum defects, while the off-diagonal terms are responsible for configuration interaction effects. Input on the form of $\mathbf{K}(\mathbf{R})$ now comes from knowledge of the corresponding BO potentials plus their derivatives with respect to bond length. As in the single-channel case, the aim is to extrapolate information from a single low principle quantum number to higher members of the series. The method involves differentiation of the electronic quantization condition, expressed in terms of $\mathbf{K}(\mathbf{R})$, rather than simple differentiation of the function $\mu(R)$. The result is an *explicit connection* between the elements of the reactance matrix corresponding to multiconfiguration Rydberg diatomic states and the relevant nonadiabatic matrix elements, adiabatic corrections, and R derivatives of the BO potentials.

II. THEORY

A. Multichannel quantum-defect theory representation of diatomic Rydberg states

It may be helpful to start by summarizing the main elements of MQDT theory for diatomic molecules, for which the electronic wave functions (WF's) Ψ_Λ, with given Λ at a fixed bond length R, is represented outside a core in the form [8,10]: [hereafter we use atomic units ($\hbar = m = e = 1$)]

$$\Psi_\Lambda(\mathbf{r},R) = \sum_{j=1}^{N} Z_j^\Lambda(R)\Psi_{\Lambda_j^+}^{BO}(\mathbf{r},R)Y_{\Lambda-\Lambda_j^+}^{l_j}(\vartheta,\varphi)e^{i\Lambda_j^+\varphi}$$

$$\times\left[f_{l_j}(\nu,r) - \sum_{j'=1}^{N} K_{jj'}^\Lambda(R)g_{l_{j'}}(\nu,r)\right], \quad r > r_c, \tag{4}$$

where most of the symbols have their conventional significance. One unfamiliar aspect may be that the sum is over channels (i.e., series converging to a given positive-ion core state) rather than over states. Secondly $f_{l_j}(\nu,r)$ and $g_{l_j}(\nu,r)$ are regular and irregular radial coulomb functions [5], where ν depends on the energy according to Eq. (6) below. $\mathbf{K}^\Lambda$ is the real symmetric reactance matrix, which is assumed to encode all the non-Coulomb Rydberg core interactions; its elements are sometimes expressed as $K_{jj'}^\Lambda = K_{j'j}^\Lambda = \tan\pi\mu_{jj'}^\Lambda$, where $\mu_{jj'}^\Lambda(R)$ are termed the *quantum defect functions* [5]. Finally the mixing coefficients Z_j^Λ represent configuration interactions between the channels.

Both $f_{l_j}(\nu,r)$ and $g_{l_j}(\nu,r)$ typically diverge exponentially as $r \to \infty$, and the mixing coefficients Z_j^Λ and BO energies $E_{\alpha,\Lambda}^{BO}(R)$ for a particular Rydberg state α are determined by elimination of these divergent terms, a procedure that leads to a quantization condition of the form [8,10]

$$[I_\alpha^\Lambda + \mathbf{K}^\Lambda]\mathbf{N}_\alpha^\Lambda = 0, \tag{5}$$

where $I_\alpha^\Lambda = \tan\pi\nu_{j\alpha}^\Lambda$ is the diagonal matrix, with energy dependent arguments such that

$$\nu_{j\alpha}^\Lambda(E,R) = \sqrt{\frac{0.5}{E_{\Lambda_j^+}^{BO}(R)-E}}. \tag{6}$$

It also proves convenient to express the above column vector in Eq. (5) as $\mathbf{N}_\alpha^\Lambda = q_\alpha^\Lambda \mathbf{Z}_\alpha^\Lambda$, where q_α^Λ is a diagonal matrix with elements [5]:

$$q_\alpha^\Lambda = (-1)^{l_j}\sqrt{\frac{2}{\pi(\nu_{j\alpha}^\Lambda)^3}}\cos\pi\nu_{j\alpha}^\Lambda. \tag{7}$$

The normalization $\mathbf{Z}_\alpha^{\Lambda^T}\mathbf{Z}_\alpha^\Lambda = 1$ applies, provided that $\mathbf{K}^\Lambda$ is independent of energy [6]. The Born-Oppenheimer electronic eigenvalues $E_{\alpha,\Lambda}^{BO}(R)$ are obtained by adjusting E in Eq. (6) to satisfy

$$\det[I_\alpha^\Lambda + \mathbf{K}^\Lambda] = 0, \tag{8}$$

and the corresponding BO eigenfunctions take the forms

$$\Psi_{\alpha,\Lambda}^{BO}(\mathbf{r},R) = \sum_{j=1}^{N} Z_{j\alpha}^\Lambda(R)\Psi_{\Lambda_j^+}^{BO}(\mathbf{r},R)P_{j\alpha}^\Lambda(\nu_{j\alpha}^\Lambda,l_j,r)$$

$$\times Y_{\Lambda-\Lambda_j^+}^{l_j}(\vartheta,\varphi)e^{i\Lambda_j^+\varphi}, \tag{9}$$

where the radial WF's $P_{j\alpha}^\Lambda$ of the remote electron may be approximated as [5]

$$P_{j\alpha}^\Lambda(\nu_{j\alpha}^\Lambda,l_j,r) = \frac{W_{\nu_{j\alpha}^\Lambda,\lambda_j+1/2}(2r/\nu_{j\alpha}^\Lambda)}{\nu_{j\alpha}^\Lambda\sqrt{\Gamma(\nu_{j\alpha}^\Lambda+\lambda_j+1)\Gamma(\nu_{j\alpha}^\Lambda-\lambda_j)}}, \tag{10}$$

where Γ and W are gamma and Whittaker functions, respectively [16], while λ_j is defined to differ from $\nu_{j\alpha}^\Lambda$ by an integer, in which case $P_{j\alpha}^\Lambda(\nu_{j\alpha}^\Lambda,l_j,r)$ remains finite as $r \to \infty$.

Simplifications apply in the degenerate case such that the core energies, $E_{\Lambda_j^+}^{BO}(R)$ of all channels are equal. In such cases diagonalization of the K matrix leads to

$$E_{\alpha,\Lambda}^{BO}(R) = E_{\Lambda^+}^{BO}(R) - \frac{1}{2(\nu_\alpha^\Lambda(R))^2}, \quad \nu_\alpha^\Lambda(R) = n$$

$$-\frac{1}{\pi}\arctan[\kappa_\alpha^\Lambda(R)], \tag{11}$$

$$\Psi_{\alpha,\Lambda}^{BO}(\mathbf{r},R) = \Psi_{\Lambda^+}^{BO}(\mathbf{r},R)e^{i\Lambda^+\varphi}\sum_{j=1}^{N} Z_{j\alpha}^\Lambda(R)P_{j\alpha}^\Lambda(\nu_\alpha^\Lambda,l_j,r)$$

$$\times Y_{\Lambda-\Lambda^+}^{l_j}(\vartheta,\varphi), \tag{12}$$

where κ_α^Λ and $\mathbf{Z}_\alpha^\Lambda$, are, respectively the eigenvalues and eigenvectors of $\mathbf{K}^\Lambda$, and n is an integer.

B. Orthogonality conditions and overlap integrals

The orthogonality between BO wave functions α and β requires that $\langle\Psi_{\alpha,\Lambda}^{BO}|\Psi_{\beta,\Lambda'}^{BO}\rangle = \delta_{\alpha\beta}$, from which it follows that

$$\delta_{\alpha\beta} = \sum_{j=1}^{N} Z_{j\alpha}^\Lambda Z_{j\beta}^{\Lambda'} S_{j\alpha\beta}^{\Lambda,\Lambda'} F_j^{\Lambda,\Lambda'}, \tag{13}$$

where $F_j^{\Lambda,\Lambda'} = \langle Y_{\Lambda-\Lambda_j^+}^{l_j}|Y_{\Lambda'-\Lambda_j^+}^{l_j}\rangle = \delta_{\Lambda,\Lambda'}$ and $S_{j\alpha\beta}^{\Lambda,\Lambda'} = \langle P_{j\alpha}^\Lambda|P_{j\beta}^{\Lambda'}\rangle$ is the radial overlap integral for the jth channel. It is seen that the states corresponding to the different Λ values always satisfy Eq. (13). Alternatively, if states α and β have a common Λ value, Eq. (5) requires that

$$\mathbf{N}_\beta^{\Lambda^T}[I_\alpha^\Lambda + \mathbf{K}^\Lambda]\mathbf{N}_\alpha^\Lambda = 0, \tag{14}$$

$$\mathbf{N}_\alpha^{\Lambda^T}[I_\beta^\Lambda + \mathbf{K}^\Lambda]\mathbf{N}_\beta^\Lambda = 0. \tag{15}$$

Subtraction of Eqs. (14) and (15) leads to

$$0 = \mathbf{N}_\beta^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\mathbf{N}_\alpha^\Lambda = \mathbf{Z}_\beta^{\Lambda^T} q_\beta^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]q_\alpha^\Lambda \mathbf{Z}_\alpha^\Lambda, \quad (16)$$

since $I_\alpha^\Lambda, I_\beta^\Lambda$ are the diagonal matrices and $\mathbf{K}^\Lambda$ is symmetric. Substitution of relations (7) and (6) on the right-hand side of Eq. (16) therefore yields

$$0 = \frac{2}{\pi} \sum_{j=1}^N Z_{j\alpha}^\Lambda Z_{j\beta}^\Lambda \frac{\sin \pi(\nu_{j\alpha}^\Lambda - \nu_{j\beta}^\Lambda)}{(\nu_{j\alpha}^\Lambda \nu_{j\beta}^\Lambda)^{3/2}}$$

$$= 2(E_{\alpha,\Lambda}^{\mathrm{BO}} - E_{\beta,\Lambda}^{\mathrm{BO}}) \sum_{j=1}^N Z_{j\alpha}^\Lambda Z_{j\beta}^\Lambda S_{j\alpha\beta}^\Lambda, \quad (17)$$

where

$$S_{j\alpha\beta}^\Lambda = 2 \frac{\sin \pi(\nu_{j\alpha}^\Lambda - \nu_{j\beta}^\Lambda) \sqrt{\nu_{j\alpha}^\Lambda \nu_{j\beta}^\Lambda}}{\pi(\nu_{j\alpha}^\Lambda - \nu_{j\beta}^\Lambda)(\nu_{j\alpha}^\Lambda + \nu_{j\beta}^\Lambda)} \quad (18)$$

since $E_{\alpha,\Lambda}^{\mathrm{BO}} \neq E_{\beta,\Lambda}^{\mathrm{BO}}$. Equation (18) demonstrates that the $S_{\alpha\beta}$ values rapidly decrease as the difference $\Delta = \nu_{j\alpha}^\Lambda - \nu_{k\beta}^\Lambda$ of the effective quantum numbers increases. It follows that the overlap integrals $S_{jk\alpha\beta}^\Lambda$ between radial WF's corresponding to the different nondegenerate core states with the same Λ^+ values ($\Lambda_j^+ = \Lambda_k^+$; $E_{\Lambda_j^+}^{\mathrm{BO}} \neq E_{\Lambda_k^+}^{\mathrm{BO}}$) should be very small for high Rydberg states, because $\Delta \sim (\nu_j \nu_k)^{3/2}(E_{\Lambda_j^+}^{\mathrm{BO}} - E_{\Lambda_k^+}^{\mathrm{BO}}) \gg 1$. It is interesting to note that Eq. (18) is very close to its one-channel counterpart [14] $S_{\alpha\beta}^{ac} = \sin \pi(\nu_\alpha - \nu_\beta)/\pi(\nu_\alpha - \nu_\beta)$, because $(\nu_\alpha + \nu_\beta)/2 \simeq \sqrt{\nu_\alpha \nu_\beta}$, although the latter is normally regarded as a semiclassical, rather than a MQDT result.

C. Multichannel quantum-defect theory analog of the Hellmann-Feynman theorem

The quantization equation (5) is the MQDT analog of the conventional electronic Schrödinger equation, which means that differentiation with respect to R can yield counterparts of the Hellmann-Feynman theorem; thus

$$[\partial I_\alpha^\Lambda + \partial \mathbf{K}^\Lambda]\mathbf{N}_\alpha^\Lambda = -[I_\alpha^\Lambda + \mathbf{K}^\Lambda]\partial \mathbf{N}_\alpha^\Lambda. \quad (19)$$

Multiplication of Eq. (19) from the left by $\mathbf{N}_\alpha^{\Lambda^T}$ yields

$$\mathbf{N}_\alpha^{\Lambda^T}\partial I_\alpha^\Lambda \mathbf{N}_\alpha^\Lambda = -\mathbf{N}_\alpha^{\Lambda^T}\partial \mathbf{K}^\Lambda \mathbf{N}_\alpha^\Lambda, \quad (20)$$

while multiplication of Eq. (19) from left by $\mathbf{N}_\beta^{\Lambda^T}$ leads to

$$\mathbf{N}_\beta^{\Lambda^T}[\partial I_\alpha^\Lambda + \partial \mathbf{K}^\Lambda]\mathbf{N}_\alpha^\Lambda = -\mathbf{N}_\beta^{\Lambda^T}[I_\alpha^\Lambda + \mathbf{K}^\Lambda]\partial \mathbf{N}_\alpha^\Lambda$$

$$= \mathbf{N}_\beta^{\Lambda^T}[I_\beta^\Lambda - I_\alpha^\Lambda]\partial \mathbf{N}_\alpha^\Lambda, \quad (21)$$

after exploiting Eq. (5) and the symmetry of $I_\alpha^\Lambda, I_\beta^\Lambda$ and the matrix $\mathbf{K}^\Lambda$. $\mathbf{K}^\Lambda$ is assumed to be independent of energy. The counterpart of Eq. (21) for the β state is

$$\mathbf{N}_\alpha^{\Lambda^T}[\partial I_\beta^\Lambda + \partial \mathbf{K}^\Lambda]\mathbf{N}_\beta^\Lambda = \mathbf{N}_\alpha^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\partial \mathbf{N}_\beta^\Lambda. \quad (22)$$

The summation and subtraction of Eqs. (21) and (22) lead, respectively, to the relations

$$\mathbf{N}_\alpha^{\Lambda^T}[\partial I_\alpha^\Lambda + \partial I_\beta^\Lambda]\mathbf{N}_\beta^\Lambda + 2\mathbf{N}_\alpha^{\Lambda^T}\partial \mathbf{K}^\Lambda \mathbf{N}_\beta^\Lambda$$

$$= \mathbf{N}_\alpha^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\partial \mathbf{N}_\beta^\Lambda - \mathbf{N}_\beta^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\partial \mathbf{N}_\alpha^\Lambda, \quad (23)$$

$$\mathbf{N}_\alpha^{\Lambda^T}[\partial I_\alpha^\Lambda - \partial I_\beta^\Lambda]\mathbf{N}_\beta^\Lambda + \mathbf{N}_\alpha^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\partial \mathbf{N}_\beta^\Lambda + \mathbf{N}_\beta^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\partial \mathbf{N}_\alpha^\Lambda$$

$$= \partial[\mathbf{N}_\alpha^{\Lambda^T}[I_\alpha^\Lambda - I_\beta^\Lambda]\mathbf{N}_\beta^\Lambda] = 0. \quad (24)$$

Equation (24) may be viewed as a corollary of the orthogonality condition (16).

Further substitution of Eqs. (7) and (6) in Eqs. (20) and (23) leads, after tedious but straightforward algebraic manipulations, to the following explicit forms:

$$\partial E_{\alpha,\Lambda}^{\mathrm{BO}} = \left[\sum_{j=1}^N (Z_{j\alpha}^\Lambda)^2 \partial E_{\Lambda_j^+}^{\mathrm{BO}} \right] - \frac{1}{2}\mathbf{Z}_\alpha^{\Lambda^T} q_\alpha^{\Lambda^T}\partial \mathbf{K}^\Lambda q_\alpha^\Lambda \mathbf{Z}_\alpha^\Lambda, \quad (25)$$

$$\sum_{j=1}^N (\partial Z_{j\beta}^\Lambda Z_{j\alpha}^\Lambda - \partial Z_{j\alpha}^\Lambda Z_{j\beta}^\Lambda)S_{j\alpha\beta}^\Lambda$$

$$= \frac{\mathbf{Z}_\alpha^{\Lambda^T} q_\alpha^{\Lambda^T}\partial \mathbf{K}^\Lambda q_\beta^\Lambda \mathbf{Z}_\beta^\Lambda}{E_{\alpha,\Lambda}^{\mathrm{BO}} - E_{\beta,\Lambda}^{\mathrm{BO}}} + 2\sum_{j=1}^N Z_{j\beta}^\Lambda Z_{j\alpha}^\Lambda$$

$$\times \left[\frac{3}{4}S_{j\alpha\beta}^\Lambda \left(\frac{\partial \nu_{j\beta}^\Lambda}{\nu_{j\beta}^\Lambda} - \frac{\partial \nu_{j\alpha}^\Lambda}{\nu_{j\alpha}^\Lambda} \right) \right.$$

$$\left. + \frac{(\partial \nu_{j\alpha}^\Lambda + \partial \nu_{j\beta}^\Lambda)\cos[\pi(\nu_{j\alpha}^\Lambda - \nu_{j\beta}^\Lambda)]\sqrt{\nu_{j\alpha}^\Lambda \nu_{j\beta}^\Lambda}}{(\nu_{j\alpha}^\Lambda - \nu_{j\beta}^\Lambda)(\nu_{j\alpha}^\Lambda + \nu_{j\beta}^\Lambda)} \right], \quad (26)$$

which are the MQDT analogs of the diagonal (1) and nondiagonal (2) Hellmann-Feynman theorems, respectively. Relation (26) will be applied to estimate the radial coupling matrix elements in Sec. II D.

D. Nonadiabatic coupling matrix elements

First, nonadiabatic matrix elements $V_{\alpha\beta}^\Lambda(R)$ between the interacting BO diatomic states α and β corresponding to the same Λ value may be expressed as [4]

$$V_{\alpha\beta}^\Lambda = 2B_{\alpha\beta}^\Lambda \partial + D_{\alpha\beta}^\Lambda + G_{\alpha\beta}^\Lambda - L_{\alpha\beta}^\Lambda/R^2, \quad (27)$$

in which $B_{\alpha\beta}^\Lambda(R) = \langle \alpha | \partial \beta \rangle$ and $D_{\alpha\beta}^\Lambda(R) = \langle \alpha | \partial^2 \beta \rangle$ are radial coupling terms [∂^2 denotes the second partial derivative with respect to R]; second, $G_{\alpha\beta}^\Lambda(R) = \langle \alpha | \mathbf{P}^2 | \beta \rangle/4$ is an electronic coupling term dependent on the total electron momentum $\mathbf{P} = \Sigma_{i=1}^M \mathbf{\nabla}_i$ ($\mathbf{\nabla}_i$ refers to differentiation with respect to the r coordinates of the ith electron, M is the total number of electrons in the molecule); finally $L_{\alpha\beta}^\Lambda(R) = \langle \alpha | L^+ L^- | \beta \rangle$ represents angular coupling, where the ladder electronic angular momentum operators $L^\pm = L_x \pm iL_y$ refer to the molecule-fixed frame. The $D_{\alpha\beta}^\Lambda$ matrix elements can be expressed through the corresponding B_{ij}^Λ values by the relation [3]: $D_{\alpha\beta}^\Lambda = [\Sigma_{i \neq \alpha, \beta}^\infty B_{\alpha i}^\Lambda B_{i\beta}^\Lambda] + \partial B_{\alpha\beta}^\Lambda$.

The first derivative of the BO WF with respect to R for the given state β is readily obtained by direct differentiation of Eq. (9):

$$\partial\Psi^{BO}_{\beta,\Lambda}=\sum_{j=1}^{N}Y^{l_j}_{\Lambda-\Lambda^+_j}e^{i\Lambda^+_j\varphi}$$

$$\times[\partial Z^{\Lambda}_{j\beta}\Psi^{BO}_{\Lambda^+_j}P^{\Lambda}_{j\beta}+Z^{\Lambda}_{j\beta}(\partial\Psi^{BO}_{\Lambda^+_j}P^{\Lambda}_{j\beta}+\Psi^{BO}_{\Lambda^+_j}\partial P^{\Lambda}_{j\beta})].$$

$$(28)$$

Multiplication of Eq. (28) from the left by the BO WF of state α approximated by Eq. (9) followed by integration over electronic coordinates yields

$$B^{\Lambda}_{\alpha\beta}=\sum_{j=1}^{N}[\partial Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}S^{\Lambda}_{j\alpha\beta}+Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}\langle P^{\Lambda}_{j\alpha}|\partial P^{\Lambda}_{j\beta}\rangle]+\mathbf{Z}^T_\alpha\mathbf{B}^c\mathbf{Z}_\beta,$$

$$(29)$$

where $S^{\Lambda}_{j\alpha\beta}$ is the overlap integral given by Eq. (18), $\mathbf{B}^c$ is the antisymmetric matrix with the nonvanishing nondiagonal elements $B^c_{k\alpha j\beta}=\langle\Psi^{BO}_{\Lambda^+_k}|\partial\Psi^{BO}_{\Lambda^+_j}\rangle S^{\Lambda}_{k\alpha j\beta}$, where $S^{\Lambda}_{k\alpha j\beta}$ $=\langle P^{\Lambda}_{k\alpha}|P^{\Lambda}_{j\beta}\rangle$ is the overlap integral between radial WF's corresponding to the different j and k channels.

One-electron operators of the momentum $\mathbf{P}$ and angular momentum $\mathbf{L}$ can be transformed to the sum V_c+V_1 $+V_{c,1}$, where the V_c,V_1 operate only on the core and the Rydberg WF's, respectively, whereas the multielectron operator $V_{c,1}$ represents mutual electron-core interactions:

$$\mathbf{P}^2=\sum_{i=1}^{M-1}\Delta_i+\Delta_1+2\sum_{i\ne1}^{M-1}\nabla_i\nabla_1,\qquad(30)$$

$$L^+L^-=L^+_cL^-_c+l^+_1l^-_1+(L^+_cl^-_1+L^-_cl^+_1).\qquad(31)$$

The tacit assumption of the conventional MQDT approximation is that matrix elements of the multielectron operators are negligible [11]. Remote electron and core contributions to the relevant matrix elements can therefore be treated additively;

$$G^{\Lambda}_{\alpha\beta}=\sum_{j=1}^{N}[Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}\langle P^{\Lambda}_{j\alpha}|\Delta_1|P^{\Lambda}_{j\beta}\rangle]+\mathbf{Z}^T_\alpha\mathbf{G}^c\mathbf{Z}_\beta,\quad(32)$$

$$L^{\Lambda}_{\alpha\beta}=\sum_{j=1}^{N}\{Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}S^{\Lambda}_{j\alpha\beta}[l_j(l_j+1)-(\Lambda-\Lambda^+_j)^2]\}+\mathbf{Z}^T_\alpha\mathbf{L}^c\mathbf{Z}_\beta,$$

$$(33)$$

where $\mathbf{G}^c$ and $\mathbf{L}^c$ are symmetric core matrices with elements $G^c_{kj\beta\alpha}=\langle\Psi^{BO}_{\Lambda^+_k}|\Sigma^{M-1}_{i=1}\Delta_i|\Psi^{BO}_{\Lambda^+_j}\rangle S^{\Lambda}_{kj\alpha\beta}$ and $L^c_{kj\beta\alpha}$ $=\langle\Psi^{BO}_{\Lambda^+_k}|L^+_cL^-_c|\Psi^{BO}_{\Lambda^+_j}\rangle S^{\Lambda}_{kj\alpha\beta}$.

It is clear that the nondiagonal matrix elements of the $\mathbf{B}^c$, $\mathbf{G}^c$, and $\mathbf{L}^c$ matrices remain finite only when $\Lambda^+_j=\Lambda^+_k$ and $l_j=l_k$. Hence, they vanish either when all core states have different electronic symmetries or when all channels belong to the same core. Moreover, even strictly nonzero off-diagonal can often be neglected in practice because the over-

lap integrals $S^{\Lambda}_{k\alpha j\beta}$ for $k\ne j$ are expected to be very small for high Rydberg states (see Sec. II B). The dominant contributions to the matrix elements (29), (32), and (33) therefore reduce to

$$G^{\Lambda}_{\alpha\beta}=\frac{1}{4}\sum_{j=1}^{N}Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}[\langle P^{\Lambda}_{j\alpha}|\Delta_1|P^{\Lambda}_{j\beta}\rangle+G^c_{jj}S^{\Lambda}_{j\alpha\beta}],\quad(34)$$

$$L^{\Lambda}_{\alpha\beta}=\sum_{j=1}^{N}Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}S^{\Lambda}_{j\alpha\beta}[l_j(l_j+1)-(\Lambda-\Lambda^+_j)^2+L^c_{jj}],$$

$$(35)$$

$$B^{\Lambda}_{\alpha\beta}=\frac{1}{2}\sum_{j=1}^{N}[(\partial Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}-\partial Z^{\Lambda}_{j\alpha}Z^{\Lambda}_{j\beta})S^{\Lambda}_{j\alpha\beta}+Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}$$

$$\times(\langle P^{\Lambda}_{j\alpha}|\partial P^{\Lambda}_{j\beta}\rangle-\langle P^{\Lambda}_{j\beta}|\partial P^{\Lambda}_{j\alpha}\rangle)]\qquad(36)$$

after use of the identity $B^{\Lambda}_{\alpha\beta}=-B^{\Lambda}_{\beta\alpha}$. Finally, substitution of Eq. (26) in Eq. (36) yields

$$B^{\Lambda}_{\alpha\beta}=\frac{\mathbf{Z}^{\Lambda T}_\alpha q^{\Lambda T}_\alpha\partial\mathbf{K}^{\Lambda}q^{\Lambda}_\beta\mathbf{Z}^{\Lambda}_\beta}{2(E^{BO}_{\alpha,\Lambda}-E^{BO}_{\beta,\Lambda})}$$

$$+\sum_{j=1}^{N}Z^{\Lambda}_{j\beta}Z^{\Lambda}_{j\alpha}\left[\frac{\langle P^{\Lambda}_{j\alpha}|\partial P^{\Lambda}_{j\beta}\rangle-\langle P^{\Lambda}_{j\beta}|\partial P^{\Lambda}_{j\alpha}\rangle}{2}\right.$$

$$+\frac{(\partial\nu^{\Lambda}_{j\alpha}+\partial\nu^{\Lambda}_{j\beta})\cos[\pi(\nu^{\Lambda}_{j\alpha}-\nu^{\Lambda}_{j\beta})]\sqrt{\nu^{\Lambda}_{j\alpha}\nu^{\Lambda}_{j\beta}}}{(\nu^{\Lambda}_{j\alpha}-\nu^{\Lambda}_{j\beta})(\nu^{\Lambda}_{j\alpha}+\nu^{\Lambda}_{j\beta})}$$

$$\left.+\frac{3}{4}S^{\Lambda}_{j\alpha\beta}\left(\frac{\partial\nu^{\Lambda}_{j\beta}}{\nu^{\Lambda}_{j\beta}}-\frac{\partial\nu^{\Lambda}_{j\alpha}}{\nu^{\Lambda}_{j\alpha}}\right)\right].\qquad(37)$$

The matrix elements $\langle P^{\Lambda}_{j\alpha}|\partial P^{\Lambda}_{j\beta}\rangle,\langle P^{\Lambda}_{j\alpha}|\Delta_1|P^{\Lambda}_{j\beta}\rangle$ between generally nonorthogonal radial WF's can either be estimated numerically using the analytical representation (10) or reduced to analytical sums over their orthogonal counterparts, as recently derived [14] in the closed form

$$\langle P^{\Lambda}_{j\alpha}|\partial P^{\Lambda}_{j\beta}\rangle=2\partial\nu^{\Lambda}_{j\beta}\sum_{\nu_{j\beta'}\ne\nu_{j\beta}}^{\infty}S^{\Lambda}_{j\alpha\beta'}\frac{\sqrt{\nu^{\Lambda}_{j\beta}\nu^{\Lambda}_{j\beta'}}}{m(\nu^{\Lambda}_{j\beta'}+\nu^{\Lambda}_{j\beta})},\quad(38)$$

$$\langle P^{\Lambda}_{j\alpha}|\Delta_1|P^{\Lambda}_{j\beta}\rangle=\sum_{\nu_{j\beta'}}^{\infty}S^{\Lambda}_{j\alpha\beta'}\left[\frac{2R\partial\nu^{\Lambda}_{j\beta}}{(\nu^{\Lambda}_{j\beta}\nu^{\Lambda}_{j\beta'})^{3/2}}\right.$$

$$\left.-\left(\frac{\nu^{\Lambda}_{j\beta'}+\nu^{\Lambda}_{j\beta}}{2\nu^{\Lambda}_{j\beta}\nu^{\Lambda}_{j\beta'}}\right)^2J_m(mx)\right].\qquad(39)$$

Here $x=\sqrt{1-(l_j+0.5)^2/(\nu^{\Lambda}_{j\beta}\nu^{\Lambda}_{j\beta'})}$, while $S^{\Lambda}_{j\alpha\beta'}$ is the overlap integral given by Eq. (18), $m=\nu^{\Lambda}_{j\beta'}-\nu^{\Lambda}_{j\beta}$ is an integer and $J_m(mx)$ is a Bessel function of order m.

E. Adiabatic correction

The adiabatic correction $A^{\Lambda}_\alpha(R)$ for a given BO electronic state α is [4]

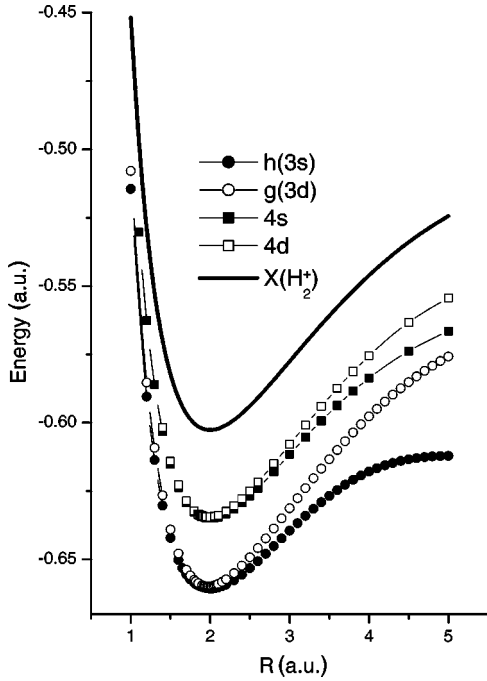FIG. 1. The *ab initio* Born-Oppenheimer potentials for the ground state of a H_2^+ ion [22] along with the g, h $^3\Sigma_g^+$ [19] and $4s$, $4d$ $^3\Sigma_g^+$ [20] states of a H_2 molecule.

$$A_\alpha^\Lambda = -\frac{1}{2m}[D_{\alpha\alpha}^\Lambda + G_{\alpha\alpha}^\Lambda - (L_{\alpha\alpha}^\Lambda - \Lambda^2)/R^2], \qquad (40)$$

where m is the reduced molecular mass. The elements $D_{\alpha\alpha}^\Lambda$ can be estimated from Eq. (37) by use of the identity: $D_{\alpha\alpha}^\Lambda = -\Sigma_{i\neq\alpha}^\infty(B_{\alpha i}^\Lambda)^2$, while $G_{\alpha\alpha}^\Lambda$ and $L_{\alpha\alpha}^\Lambda$ are readily obtained from Eqs. (34) and (35), respectively,

$$G_{\alpha\alpha}^\Lambda = \frac{1}{4}\sum_{j=1}^N (Z_{j\alpha}^\Lambda)^2[\langle P_{j\alpha}^\Lambda|\Delta_1|P_{j\alpha}^\Lambda\rangle + G_{jj}^c], \qquad (41)$$

$$L_{\alpha\alpha}^\Lambda = \sum_{j=1}^N (Z_{j\alpha}^\Lambda)^2[l_j(l_j+1) - (\Lambda-\Lambda_j^+)^2 + L_{jj}^c]. \quad (42)$$

Hence, the total adiabatic correction A_α^Λ for a given Rydberg state α is reduced to

$$A_\alpha^\Lambda = \frac{1}{2m}\left[\sum_{i\neq\alpha}^\infty (B_{\alpha i}^\Lambda)^2 + \sum_{j=1}^N (Z_{j\alpha}^\Lambda)^2\left(\frac{\nu_{j\alpha}^\Lambda - 2R\partial\nu_{j\alpha}^\Lambda}{4(\nu_{j\alpha}^\Lambda)^3} - \frac{G_{jj}^c}{4}\right.\right.$$
$$\left.\left. + \frac{L_{jj}^c - \Lambda^2 + l_j(l_j+1) - (\Lambda-\Lambda_j^+)^2}{R^2}\right)\right], \qquad (43)$$

where hypervirial theorem was applied to estimate the diagonal matrix element $\langle P_{j\alpha}^\Lambda|\Delta_1|P_{j\alpha}^\Lambda\rangle$.

III. APPLICATION TO $H_2 s,d\,^3\Sigma_g^+$ COMPLEX

The validity of the above approximations are tested below by calculations of the nonadiabatic matrix elements and adiabatic corrections for the g,h $^3\Sigma_g^+$ and $4s,4d$ $^3\Sigma_g^+$ states of

molecular hydrogen, which correspond to the first members ($n=3$ for the g, h and $n=4$ for the $4s,4d$ states) of the triplet s,d $^3\Sigma_g^+$ Rydberg series (see Fig. 1). These electronic states are chosen for the following reasons.

(1) The BO states of the $H_2 s,d$ $^3\Sigma_g^+$ complex were found to be represented, at small and intermediate internuclear distances, by the pair of the l-mixing diabatic s and d series converging to the ground state of H_2^+ : s:$(1\sigma_g)ns\sigma_g$; d:$(1\sigma_g)nd\sigma_g$ [11]. Since the present Rydberg states have the same core, the relevant matrix elements are simplified significantly (see the Appendix).

(2) Strong nonadiabatic interactions between the states of the complex are expected to occur near the equilibrium distances of their potential curves (see Fig. 1), and the relevant *ab initio* estimates of nonadiabatic radial and angular coupling matrix elements are known for the g,h $^3\Sigma_g^+$ states [17,18].

(3) Highly accurate *ab initio* BO potential curves and their derivatives with respect to R, together with adiabatic corrections have been recently calculated for g,h $^3\Sigma_g^+$ [19] and $4s,4d$ $^3\Sigma_g^+$ [20] states, by use of explicitly correlated wave functions in elliptic coordinates.

A. Determination of the reactance matrix

Elements of reactance matrix were derived by nonlinear least-squares fitting to the *ab initio* BO curves $E_{\alpha,ab}^{BO}$ for the lowest members of the s,d Rydberg series. Since both ∂E_α^{BO} and $B_{\alpha\beta}$ functions are proportional to $\partial\mathbf{K}$ [compare relations (25) and (37)], the highly accurate derivatives of *ab initio* BO potentials $\partial E_{\alpha,ab}^{BO}$ calculated by the hypervirial theorem in Refs. [19], [20] were simultaneously optimized along with the corresponding BO potentials in the fitting procedure for the functions $\mu_{ij}(R)$:

$$\min \sum_{i=s,d} \sum_{R_x}^M [(E_{i,ab}^{BO} - E_{i,MQDT}^{BO})^2 + (E_{i,ab}^{BO} - \partial E_{i,MQDT}^{BO})^2].$$
$$(44)$$

The diagonal μ_{ss} and μ_{dd} functions were approximated by appropriate polynomial functions of R while a more flexible pointwise representation combined with spline interpolation was used for the nondiagonal μ_{sd} values. The MQDT energy and its derivative were calculated by the analytical relations (A1) and (A2) given in the Appendix. The number M of the mesh points R_x was chosen to be larger than a number of the adjustable fitting parameters. A minimum functional (44) was sought by the modified Levenberg–Marquardt algorithm combined with a finite-difference approximation to the corresponding Jacobian matrix. The required μ_{ss}, μ_{dd}, and μ_{sd} functions were obtained from the separate fits of the g,h $^3\Sigma_g^+$ and $4s,4d$ $^3\Sigma_g^+$ pair states to clarify their dependence on principal quantum number n. The resulting quantum-defect matrices shown in Fig. 2 reproduce the *ab initio* BO curves for the g,h $^3\Sigma_g^+$ and $4s,4d$ $^3\Sigma_g^+$ states
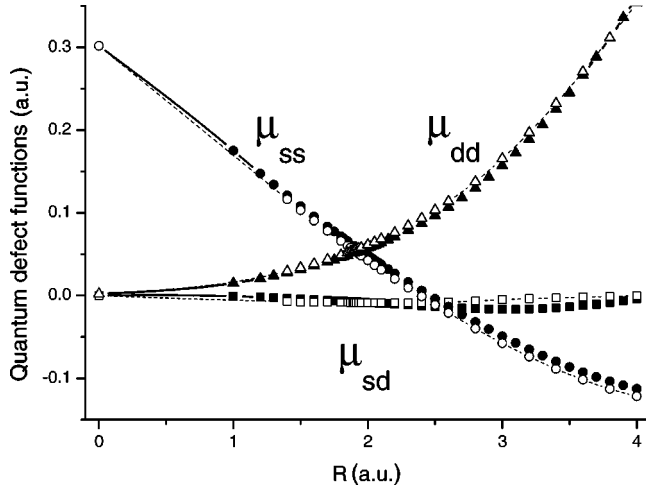
FIG. 2. The quantum-defect functions of the reactance matrix for the g, h $^3\Sigma_g^+$ [19] (solid symbols) and $4s$, $4d$ $^3\Sigma_g^+$ [20] (open symbols) states of H_2.

along with their first R derivatives to better than 10^{-5} a.u. in the region $R = 1-4$ a.u. It must be stressed that use of R derivatives of the potentials in the fitting greatly improved the accuracy of the extracted reactance matrix. As expected, the n dependence of the quantum-defect functions is very small but not quite negligible. The observed small difference of the reactance matrices corresponding to $n = 3$ and $n = 4$ may arise either from a true weak energy dependence or from a small convergence error in the *ab initio* calculations [19,20].

B. Comparison between *ab initio* and multichannel quantum-defect theory nonadiabatic coupling elements

The derived quantum-defect functions together with two-channel simplifications of the foregoing analytical formulas (A3) and (A4), given in the Appendix, were numerically tested by calculation of nonadiabatic radial and angular coupling matrix elements for the g,h $^3\Sigma_g^+$ states. The results shown in Figs. 3 and 4 demonstrate that the present MQDT estimates agree well with *ab initio* results obtained by the conventional full-configuration-interaction method with two different Gaussian type orbital (GTO) basis sets [17,18]. It should be noted that the *ab initio* data [17] seem to be more reliable than the comparable data from Ref. [18] because the former are based on more extensive GTO basis set calculations. The results presented in Figs. 3 and 5 show that the radial coupling matrix elements between the states corresponding to the same principal quantum numbers are larger than those corresponding to different n values.

The reliability of the derived quantum-defect functions and the power of the present MQDT approach are the most clearly seen in Fig. 6 where the MQDT adiabatic corrections calculated by the Eq. (A5) for the g,h $^3\Sigma_g^+$ and $4s,4d$ $^3\Sigma_g^+$ states of the H_2 molecule are compared with the highly accurate *ab initio* counterparts given in Refs. [19], [20]. The excellent agreement between the MQDT and *ab initio* adiabatic corrections for all states treated confirms the high accuracy of the derived radial matrix elements, since the posi-
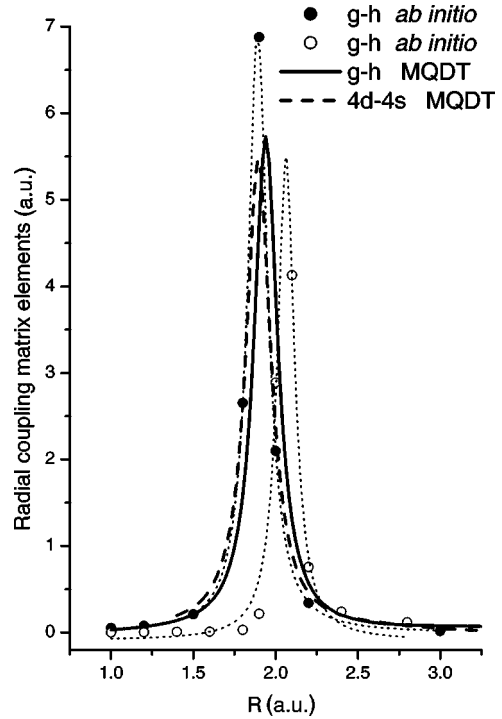

FIG. 3. The radial coupling matrix elements for the $g - h$ and $4s - 4d$ pairs of the interacted states of H_2. *Ab initio* data evaluated by the finite-difference technique were borrowed from Ref. [17] (solid circles) and Ref. [18] (open circles), respectively.

tion and height of the sharp maximum of the $A_s(R)$ and $A_d(R)$ functions are mainly determined by a sum of squares of the corresponding $B_{\alpha\beta}^\Lambda$ values [see Eq. (A5)].

IV. CONCLUSIONS

Analytical approximations for adiabatic correction and nonadiabatic matrix elements were derived and tested for the g,h $^3\Sigma_g^+$ and $4s,4d$ $^3\Sigma_g^+$ states of molecular hydrogen. The
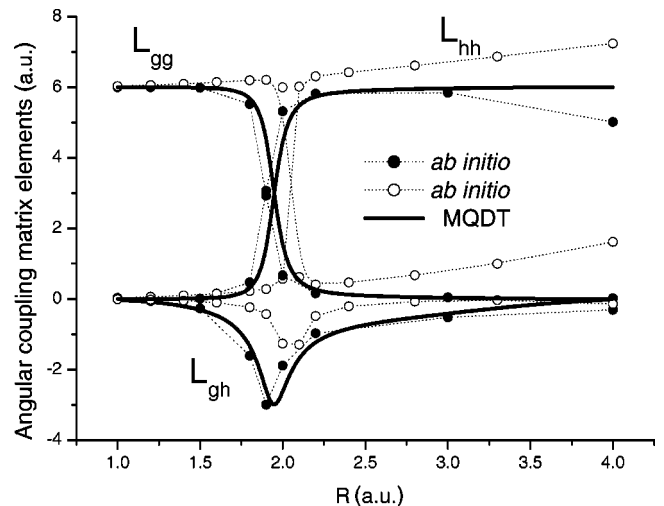

FIG. 4. The diagonal and nondiagonal matrix elements of the angular coupling for the g, h states of H_2. *Ab initio* data were taken from Ref. [17] (solid circles) and Ref. [18] (open circles).
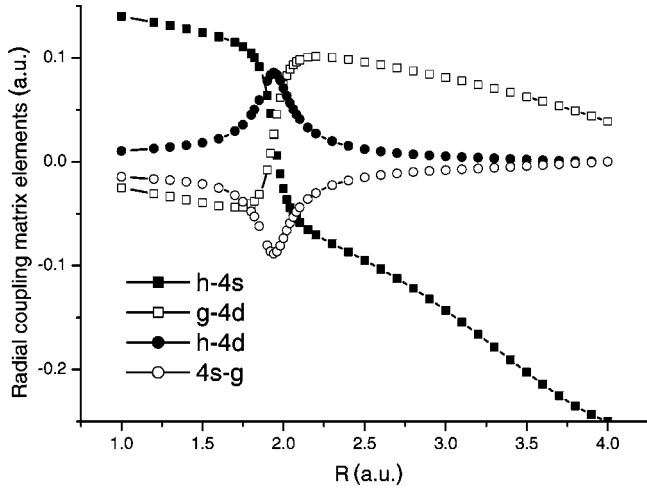
FIG. 5. The MQDT matrix elements of the radial coupling for the $h-4s$, $g-4d$, $h-4d$, and $4s-g$ pairs of H_2.

MQDT analogs of the diagonal (25) and nondiagonal (37) forms of Hellmann-Feynman theorem allow one to relate both the first derivative of the Born-Oppenheimer energy and the nonadiabatic radial coupling matrix elements for multiconfiguration Rydberg diatomic states to the first derivatives of the relevant reactance matrix in explicit forms, of which simplified two-channel versions are given in the appendix. Overall good agreement between the present MQDT estimates of the radial and angular coupling matrix elements of the g,h $^3\Sigma_g^+$ states and their *ab initio* counterparts is observed. This excellent agreement of the MQDT and *ab initio* adiabatic corrections for all states studied has been achieved by simultaneous fitting of the reactance matrix to the highly
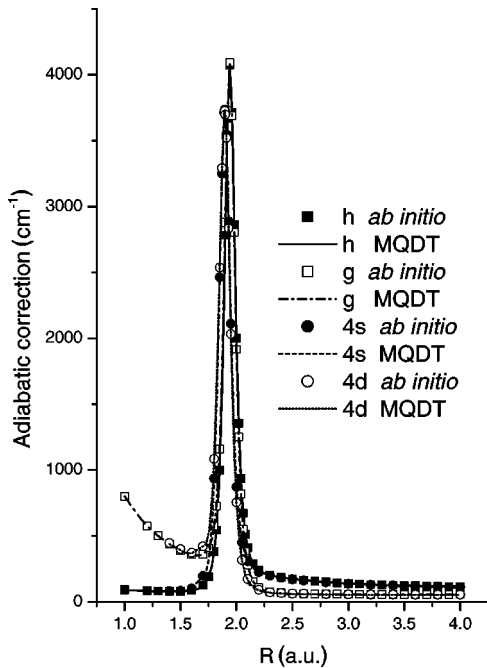

FIG. 6. A comparison of the MQDT adiabatic correction functions for the *h, g, 4s,* and *4d* states of H_2 with their high-accurate *ab initio* counterparts [19,20].

accurate *ab initio* BO potentials and their derivatives with respect to R.

The main advantage of the present approach in a comparison with the conventional MQDT method [11] is that it provides an *explicit form* for the adiabatic and nonadiabatic electronic matrix elements for all members of a given Rydberg series. It allows one to do the following:

(1) test directly the validity of MQDT approximation for a particular Rydberg electronic state at any internuclear distance by their comparison with available *ab initio* data;

(2) apply accurate *ab initio* data on derivatives of BO potentials, radial coupling matrix elements, and adiabatic corrections, which are usually known for low-lying electronic states, to refine matrix elements of the reactance matrix;

(3) incorporate the formula applications to higher members of the Rydberg series and more accurate *ab initio* data for low-lying valence electronic states on a common channel coupling, variation, or perturbation theory calculations.

APPENDIX: TWO-CHANNEL APPROXIMATION: DEGENERATE CASE

Since both members of the $H_2 s,d$ $^3\Sigma_g^+$ complex have the same core, the BO energy and WF's of the corresponding states can be approximated by using of relations (11) and (12) in the form

$$E_{s/d}^{BO} = E_{\Lambda^+}^{BO} - \frac{1}{2\nu_{s/d}^2}, \quad \nu_{s/d} = n - \bar{\mu}_{s/d},$$

$$2\tan\pi\bar{\mu}_{s/d} = (R_{ss} + R_{dd}) \pm \sqrt{(R_{ss} - R_{dd})^2 + 4R_{sd}^2},$$

$$\Psi_s^{BO} = \Psi_{\Lambda^+}^{BO}[F_s \cos\theta - F_d \sin\theta], \tag{A1}$$

$$\Psi_d^{BO} = \Psi_{\Lambda^+}^{BO}[F_s \sin\theta + F_d \cos\theta], \quad \tan 2\theta = \frac{2R_{sd}}{R_{ss} - R_{dd}},$$

where $R_{ss} = \tan\pi\mu_{ss}$, $R_{dd} = \tan\pi\mu_{dd}$, and $R_{sd} = R_{ds} = \tan\pi\mu_{sd}$, the quantities μ_{ss}, μ_{dd}, and μ_{sd} being, respectively, the quantum-defect functions for s,d channels plus the interaction between them. $E_{\Lambda^+}^{BO}$ and $\Psi_{\Lambda^+}^{BO}$ are BO energy and WF of the ground state of hydrogen ion, and F_s, F_d are wave functions of the remote electron in s,d channels, respectively. Use of the trigonometric functions in θ for the

mixing coefficients $\mathbf{Z}$ allows one to assume that θ is independent of the principal quantum numbers n if $\mathbf{K}$ is assumed to be independent of energy.

The general formulas derived in Sec. II are found to reduce to closed forms in this two state, common core model. For example, Eq. (25) shows that

$$\partial E_s^{\mathrm{BO}} = \partial E_{\Lambda^+}^{\mathrm{BO}} + \frac{\cos^2 \pi \nu_s}{\nu_s^3}$$

$$\times [K_{ss} \cos^2 \theta + K_{dd} \sin^2 \theta - K_{sd} \sin 2\theta],$$

$$\partial E_d^{\mathrm{BO}} = \partial E_{\Lambda^+}^{\mathrm{BO}} + \frac{\cos^2 \pi \nu_d}{\nu_d^3}$$

$$\times [K_{ss} \sin^2 \theta + K_{dd} \cos^2 \theta + K_{sd} \sin 2\theta] \tag{A2}$$

where

$$K_{ss} = \frac{\partial \mu_{ss}}{\cos^2 \pi \mu_{ss}}, \quad K_{dd} = \frac{\partial \mu_{dd}}{\cos^2 \pi \mu_{dd}}, \quad K_{sd} = \frac{\partial \mu_{sd}}{\cos^2 \pi \mu_{sd}}.$$

The radial coupling matrix elements between s and d states follow directly from Eq. (37):

$$B_{sd} = \frac{\sqrt{\nu_s \nu_d}}{\nu_d^2 - \nu_s^2} \cos \pi \nu_s \cos \pi \nu_d [(K_{ss} - K_{dd}) \sin 2\theta$$

$$+ 2K_{sd} \cos 2\theta],$$

$$B_{ss'} = \partial \nu_s \frac{2\sqrt{\nu_s \nu_{s'}}}{\nu_{s'}^2 - \nu_s^2}, \quad B_{sd'} = \partial \nu_d \frac{2\sqrt{\nu_d \nu_{d'}}}{\nu_{d'}^2 - \nu_d^2}. \tag{A3}$$

In addition the matrix elements between different members of the same diabatic Rydberg series $B_{ss'}$ and $B_{dd'}$ are equivalent to their one-channel counterparts [14]. The angular coupling matrix elements between s and d states are derived from Eq. (35):

$$L_{sd} = -6 \frac{\sin[\pi(\nu_s - \nu_d)]\sqrt{\nu_s \nu_d}}{\pi(\nu_s^2 - \nu_d^2)} \sin 2\theta,$$

$$L_{ss'} = 6 \sin^2 \theta, \quad L_{dd'} = 6 \cos^2 \theta, \tag{A4}$$

since $l_s = 0$ and $l_d = 2$. The adiabatic correction comes from the relation (43):

$$A_s = \left[A_{\mathrm{ion}} + \sum_{i \neq s}^{\infty} B_{si}^2 + \frac{\nu_s - 2R\partial \nu_s}{4\nu_s^3} + \frac{6\sin^2 \theta}{R^2} \right] / 2m_{\mathrm{H_2}},$$

$$A_d = \left[A_{\mathrm{ion}} + \sum_{i \neq d}^{\infty} B_{di}^2 + \frac{\nu_d - 2R\partial \nu_d}{4\nu_d^3} + \frac{6\cos^2 \theta}{R^2} \right] / 2m_{\mathrm{H_2}}, \tag{A5}$$

where $m_{\mathrm{H_2}}$ is the reduced mass of hydrogen molecular and $A_{\mathrm{ion}} = L_{\mathrm{ion}}/R^2 - G_{\mathrm{ion}}/4$. G_{ion} and L_{ion} are the known electronic and angular adiabatic matrix elements for the ground state of hydrogen ion, respectively [21,22].

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