THE RETARDATION (OR CASIMIR) POTENTIAL FOR THE RYDBERG HYDROGEN MOLECULE

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Abstract

The retardation (or Casimir) potential for Rydberg H₂—a hydrogen molecule with one electron in a highly excited, hydrogen-atom-like, electronic state and an H²⁺ core—is determined using time-dependent quantum electrodynamics in the Coulomb gauge. The potential obtained is valid over a range of r, the Rydberg electron-core separation, from several a₀ to infinity, and accurate numerical results for the magnitude of the corresponding energy shift are calculated using a discrete representation of the electric dipole oscillator strength spectrum. The prospects for measurement are analyzed.

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I. INTRODUCTION

Over the last several decades there have been many experimental and theoretical efforts devoted to the quantititative verification of a retardation effect—the change arising, due to the finite speed of propagation of light—formally, one evaluates the contribution from the exchange of two virtual photons—in the form of the interaction potential between two polarizable systems as their separation tends to asymptotic distance.

The qualitative behavior of the retardation (or Casimir) potential is known on theoretical grounds to be a change in the long-range potential power law, see, for example, Refs. [1–5]. The potentials are known for many pairs of systems, including atom-atom, atom-wall (conducting or permeable) (Ref. [6] and references therein to the original papers), electron-ion, and wall-wall. (We shall be referring to the electric dipole component of the retardation potential; for some pairs of systems the retardation potential is known for all orders of multipole, electric and magnetic [7].) There have been experimental investigations that have yielded quantitative evidence that is rather good for the effect for the wall-wall case [8,9] and even better for the atom-wall [10,11] case, and studies are underway in the atom-atom case [12]. The highest relative precision obtained thus far in a system without walls would seem to be that for the Rydberg helium atom—a He atom with one electron in a highly excited, near hydrogenic, state with \( n = 10 \), and \( l \sim n \), with a 1s \( \text{He}^+ \) core [13]. Further, it would seem to be possible to greatly increase the accuracy for the Rydberg helium atom. It can be difficult to isolate the asymptotic part of the potential in a measurement. Indeed, on theoretical grounds the form of the retardation potential is usually known over a range of \( r \), the distance between the systems, from several \( a_0 \) to infinity. The most dramatic effect of retardation is the change at asymptotic distances in the power law of the potential, but there are also effects at smaller distances.

Although Rydberg helium and a number of Rydberg helium-like ions (\( ^{12}\text{C}^+ \), \( ^{16}\text{O}^+ \), ...) have obvious merits, such as the absence of nuclear spin, a one-electron core, hydrogen-like wave functions for both electrons, etc., there are other analogous systems that offer considerable simplicity, which is essential if highly accurate theoretical results are to be obtained, and for which precise spectroscopic measurements are possible. One such system is the Rydberg hydrogen molecule, a hydrogen molecule with one electron in a highly excited, hydrogen-atom-like, electronic state and an \( \text{H}_2^+ \) core, which, like the Rydberg helium atom, has only two electrons, and for which a series of experiments have demonstrated [14] that precise resolution of electron-\( \text{H}_2^+ \) long-range forces from spectroscopic measurements is achievable. From the theoretical point of view, the \( \text{H}_2^+ \) core has some additional complexity relative to Rydberg helium, namely, the presence of nuclear spin and core rotation, but it should be possible to overcome these difficulties as it becomes necessary.

Using semi-classical theory, we recently derived the exact asymptotic form for the retardation interactions in Rydberg \( \text{H}_2 \) (the result is applicable also to the case of a Rydberg atom with a \( P \) state core). The result obtained [15] was,

\[
V(r, \theta) \sim \frac{\hbar e^2}{\pi mc_0^2} [\frac{11}{4} \alpha_s(0) + \frac{25}{12} \alpha_t(0)P_2(\cos \theta)], \quad r \sim \infty, \tag{1.1}
\]

where \( \alpha_s(0) \) and \( \alpha_t(0) \) are, respectively, the components of the static scalar and tensor electric dipole polarizabilities of the \( \text{H}_2^+ \) core, to be defined in detail later, \( r = |r| \) is the distance
of the Rydberg electron from the center of mass of the nuclei, and $\theta$ is the polar angle of the Rydberg electron with respect to the internuclear axis. There is a previous calculation of a retardation potential for two asymmetric systems—the asymptotic interaction between two neutral diatomic molecules, one or both of which could be asymmetric, was obtained by Craig and Power [16]. That analysis is not applicable to the $e^- - H_2^+$ system since the constituents are charged. In this paper, we generalize a prior calculation for the Rydberg He atom carried out using time-dependent perturbation theory in the Coulomb gauge [17,18] to the Rydberg $H_2$ system to obtain the retardation potential. The potential to be obtained has as its asymptotic limit the form Eq. (1.1) and is valid for a range of $r$ from several $a_0$ to infinity. We also obtain accurate numerical estimates of the energy shift caused by the potential.

II. EXTENSION OF A PREVIOUS CALCULATION TO A CYLINDRICALLY SYMMETRIC CORE

The retardation potential for Rydberg $H_2$ obtained in [15] using a physical argument and exhibited in Eq. (1.1) above can also be obtained using the formal apparatus of quantum electrodynamics (QED). In this section, a derivation [17,18] of the retardation potential for a Rydberg electron in helium that used nonrelativistic QED in the Coulomb gauge will be extended to the Rydberg $H_2$ system. The result to be obtained has Eq. (1.1) as its limit for $r \to \infty$ and is valid for all $r$ greater than several $a_0$. The essential modification is to allow the core to be cylindrically symmetric, since He$^+$ is being replaced by $H_2^+$. The notation used will follow closely that of [18], designated as paper I, and references to equations therein will be preceded by the symbol I, see also [17]. Many of the mathematical steps taken in reducing the virtual photon exchange matrix elements to an effective potential are similar to the spherically symmetric core case—the only modification being the core asymmetry—and the notation and symbols used for the present derivation will be analogous to those used for the spherical case where possible. Thus, for example, with $\sum_u$ representing an infinite sum and continuum integration, the essential quantity that characterized the core for Rydberg helium, the dynamic electric dipole polarizability defined in Eq. I-(2.7), was

$$\alpha_d(k) = \frac{2}{3} e^2 \sum_u \frac{|\langle 0 | r_1 | u \rangle|^2 E_{u0}}{E_{u0}^2 - E_k^2}, \quad (2.1)$$

where the wave function $|0\rangle$ and energy $E_0$ referred to the 1s state hydrogen-like He$^+$ core electron and the wave function $|u\rangle$ and energy $E_u$ referred to an intermediate $p$-state, $E_{u0} \equiv E_u - E_0$, $r_1$ was the position vector of the core electron from the nucleus, and $E_k = \hbar c k$ was the photon energy. For Rydberg $H_2$ the analogous quantity is

$$\alpha_{ij}(k) = 2e^2 \sum_u \frac{|\langle 0 | x_{1i} | u \rangle |\langle u | x_{1j} | 0 \rangle| E_{u0}}{E_{u0}^2 - E_k^2}, \quad (2.2)$$

where in the molecule-fixed frame (fixed with the core) $|0\rangle$ represents the $H_2^+$ core ground 1s$\sigma_g$ electronic state, $|u\rangle$ is an intermediate $\sigma_u$ or $\pi_u$ state, and $x_{1i}$ is the Cartesian component of the position vector of the core electron from the center of mass of the nuclei, $E_0$ and $E_u$ are the energies associated with the new $|0\rangle$ and $|u\rangle$ states, $E_{u0} = E_u - E_0$, and $E_k = \hbar c k$.
is again the photon energy. (We will use the Born-Oppenheimer approximation for \(|0\rangle\) and \(|u\rangle\).) Thus, \(\alpha_{ij}(k)\) for \(\Pi_j^+\) is the analog of \(\alpha_{ij}(k)\) for \(\text{He}^+\). [For \(|0\rangle\) in Eq. (2.2) spherically symmetric, \(\alpha_{ij}(k)\) reduces to \(\alpha_{ij}(k)\delta_{ij}\).]

Implicit in the definitions of the core parameters is their dependence on the internuclear separation \(R\). For notational convenience, this dependence will be suppressed until the last section of the paper, Sec. III B, where the matrix element over the wave function corresponding to the nuclear motion is evaluated.

There are a number of interactions due to the static multipole terms, such as the permanent quadrupole moment of the core, which we do not address in this paper, but it should be noted that they are significant. Expressions for the potentials arising from such terms have been given [19,20].

### A. The evaluation of \(V_{II}\)

After the Coulomb and permanent moment interactions, the leading term in the interaction potential between a charge and a molecular ion is due to the polarization of the molecule by the electron electric field (sometimes called the adiabatic polarization potential) and is given by, for example, Buckingham [19]. In this section, we show, briefly, how the computation of I-Sec.IV.A for the exchange of two Coulomb or instantaneous “II” photons, extended to Rydberg \(\Pi_2\), yields the leading electric dipole adiabatic term and nonadiabatic terms of higher order.

Carrying out the analog of the computation of I-Appendix A, we find for the II contribution to the effective potential

\[
V_{II}(r) = -e^4 \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{u,v} (0n | x_{1i} x_{2j} r^{-3} | uv) (uv | x_{1i} x_{2j} r^{-3} | 0n) \frac{E_u + E_v}{E_{0u} + E_{0v}}.
\]

(2.3)

The quantities \(|0\rangle\), \(|u\rangle\), \(E_{0u}\), \(x_{1i}\), and \(r = |r|\) were defined above, \(|n\rangle\) represents the hydrogen-like wave function of the Rydberg electron bound to a nucleus of charge \(Z - 1\) and in the state \(nl\) with energy \(E_n\), and \(|v\rangle\) represents an intermediate state of the Rydberg electron with an energy \(E_v\), \(E_{0n} \equiv E_v - E_n\), and \(x_j\) is a Cartesian component of \(r\).

Expanding the denominator of Eq. (2.3) in powers of \(E_{0n}/E_{0u}\), the first term, \(1/E_{0u}\), yields the adiabatic polarization potential

\[
V_{\text{pol}}(r) \equiv -\frac{1}{2} e^2 \sum_{i=1}^{3} \sum_{j=1}^{3} \alpha_{ij}(0) \hat{x}_i \hat{x}_j / r^4,
\]

(2.4)

where \(\hat{x}_1\), \(\hat{x}_2\), and \(\hat{x}_3\) are the components of the unit vector \(r/r\) in the molecule-fixed frame, that is, direction cosines, (not unit vectors).

The next term in the denominator expansion, \(-E_{0n}/E_{0u}^2\), yields, after some manipulation, the nonadiabatic potential

\[
V_{\text{nonad}}(r) \equiv \sum_{i=1}^{3} \sum_{j=1}^{3} \frac{e^2}{2r^6} \left( \delta_{ij} + 3 \hat{x}_i \hat{x}_j \right),
\]

(2.5)

where
\[ \beta_{ij} \equiv e^4 \sum_u \frac{\langle 0 | x_{1i} | u \rangle \langle u | x_{1j} | 0 \rangle}{E_{u0}^2}. \]  

(2.6)

In deriving Eq. (2.5) we follow Eq. (A7) of Ref. [17] and write

\[ \sum_v \langle n | x_{ir}^{-3} | v \rangle \langle v | x_{jr}^{-3} | n \rangle E_{vn} = \frac{3}{2} \langle n | x_{ir}^{-3} | T_2, x_{jr}^{-3} | n \rangle + \langle x_{ir}^{-3}, T_2 | x_{jr}^{-3} | n \rangle, \]  

(2.7)

where \( T_2 = \frac{p^2}{2m} \) is the kinetic energy of the Rydberg electron, and use the fact that \( \beta_{ij} = \beta_{ji} \). We found that with this technique there was no need to integrate by parts to obtain the \( r^{-6} \) dependence, as is sometimes done.

Our \( \beta_{ij} \) is the analog of \( \beta_{\text{nonad}} \) for helium [17] and reduces to \( \beta_{\text{nonad}} \delta_{ij} \) for \( |0\) \) spherically symmetric. There unfortunately exist many different definitions of \( \beta_{\text{nonad}} \) for atoms, and the same is true for \( \beta_{ij} \); we note that the definition of \( \beta_{ij} \) of Lundeen and collaborators is a factor of two larger than ours and correspondingly a factor of \( \frac{1}{2} \) appears in their expression for this potential, see Eq. (35) of [20] and our Eq. (3.38) below.

Our analysis of \( V_{IT} \) in paper I indicates that there should be an additional nonadiabatic potential of \( O(r^{-7}) \), see I-Eq.(4.12), a potential proportional to the quantity

\[ \gamma_{ij}(0) = \frac{1}{8} \left( \frac{h}{mc} \right)^2 \frac{d^2 \alpha_{ij}(k)}{dk^2} \bigg|_{k=0} \]  

(2.8)

arising from the third term, \( E_{vn}^2 / E_{u0}^3 \), in the expansion of the denominator of Eq. (2.3). Such a potential apparently has not been included in the \( e^- - H_2^+ \) potential calculations that have gone to order \( 1/r^2 \) [14,21]. We hope to present an expression for this potential in a future paper.

For a hydrogen-like ion (core) \( \alpha_d(0) = \frac{9}{4} Z^{-4} a_0^3 \), \( \beta_{\text{nonad}}(0) = \frac{43}{8} Z^{-6} a_0^5 \), and \( \gamma(0) = \frac{319}{48} Z^{-8} a_0^7 \), while for \( H_2^+ \) no such rational forms are available and the quantities depend on the internuclear distance \( R \). We return to the question of numerical values for the various polarizabilities and the energy shifts arising from Eq. (2.3) in Sec. III B below.

**B. The evaluation of \( V_{IT} \)**

Carrying out the analog of the computation of I-Sec.IV.B for the effective potential for exchange of one instantaneous and one transverse photon "IT", we find

\[ V_{IT}(r) = \frac{2e^2 h}{\pi mc r^3} \sum_{i=1}^{3} \sum_{j=1}^{3} \int_0^\infty k F_{ij}(k) J_{ij}(kr) dk \]  

(2.9)

with

\[ J_{ij}(kr) = \delta_{ij} \left[ -\frac{3}{8} j_0(kr) + \frac{1}{6} j_2(kr) \right] + 3 \hat{z}_i \hat{z}_j \left[ \frac{1}{8} j_0(kr) + \frac{1}{6} j_2(kr) \right], \]  

(2.10)

where \( j_0 \) and \( j_2 \) are spherical Bessel functions and

\[ F_{ij}(k) = 2e^2 \sum_u \frac{\langle 0 | x_{1i} | u \rangle \langle u | x_{1j} | 0 \rangle}{E_{u0} + E_k}. \]  

(2.11)
C. The evaluation of $V_{TT}$

The analog of the computation of I-Sec.IV.C for the effective potential for the exchange of two transverse photons "TT", is found to be, on inserting a convergence factor as in I,

$$V_{TT}(r) = \frac{2 e^2}{9 \pi^2 m c^2} \lim_{\mu \to 0} \sum_{i=1}^{3} \sum_{j=1}^{3} \int_{0}^{\infty} dk k^4 e^{-\mu k} H_{ij}(kr) G_{ij}(kr)$$

with

$$H_{ij}(k) = 2e^2 \sum_{u} \frac{\langle 0 | x_{i1} | u \rangle \langle u | x_{1j} | 0 \rangle E_{u0}}{E_{u0} + E_k}$$

and\(^1\)

$$G_{ij}(kr) = \frac{1}{k} P \int_{0}^{\infty} dk' \frac{k'^2}{k^2 - k'^2} \{4j_0(kr)j_0(k'r)\delta_{ij} - 2[j_0(kr)j_2(k'r) + j_2(kr)j_0(k'r)](\delta_{ij} - 3\hat{x}_i\hat{x}_j) + j_2(kr)j_2(k'r)(\delta_{ij} + 3\hat{x}_i\hat{x}_j)\},$$

where $P$ represents the Cauchy principal value. Integrating over $k'$ as in I, we find, with $s = kr$,

$$G_{ij}(s) = \frac{3}{2}\pi\{\{[-2j_0(s) + j_2(s)]s^{-3} - 3I_d(s)\}\delta_{ij} + \{(2j_0(s) + j_2(s))s^{-3} - I_p(s)\}3\hat{x}_i\hat{x}_j\},$$

where

$$I_d(s) = \frac{1}{2} \sin(2s)(s^{-2} - 3s^{-4} + s^{-6}) + \cos(2s)(s^{-3} - s^{-5}),$$

and

$$I_p(s) = \frac{1}{2} \sin(2s)(-s^{-2} - s^{-4} + 3s^{-6}) + \cos(2s)(-s^{-3} - 3s^{-5}).$$

Using the identity

$$\frac{E_{u0}}{E_{u0} + E_k} = 1 - [E_k/(E_{u0} + E_k)]$$

in $H_{ij}(k)$, the integrations arising from the "1" in Eq. (2.18) separately vanish, and using Eqs. (2.15) and (2.11) we can write

$$V_{TT}(r) = \frac{-2e^2}{\pi mc} \lim_{\mu \to 0} \sum_{i=1}^{3} \sum_{j=1}^{3} \int_{0}^{\infty} dk k^4 e^{-\mu k} F_{ij}(k)(-3/2[I_d(kr)\delta_{ij} + I_p(kr)\hat{x}_i\hat{x}_j] + 1/k^3 r^3)J_{ij}(kr).$$

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\(^1\)There is a typographical error in Eq. I-(4.24); there should be a factor $k'^2$ in the numerator.
D. The sum $V_T$ of $V_{TT}$ and $V_{TT}$

Using Eqs. (2.9) and (2.19), we can write

$$V_T(r) = V_{TT}(r) + V_{TT}(r) = \frac{e^2 \hbar}{mc} \lim_{\mu \to 0} \sum_{i=1}^{3} \sum_{j=1}^{3} \int_{0}^{\infty} dk k^4 e^{-\mu k} F_{ij}(k) [\delta_{ij} I_d(kr) + \hat{x}_i \hat{x}_j I_p(kr)].$$

(2.20)

With the replacement of $F_{ij}(k)$ by $\alpha_{ij}(k)$, Eq. (2.20) above is identical to Eqs. (2.17) and (3.16) obtained in Ref. [15] using a semi-classical argument. We will return to this point in the last section.

To facilitate comparison with the asymptotic form of the potential we introduce

$$\tilde{V}_\infty(r) = \sum_{i=1}^{3} \sum_{j=1}^{3} \left\{ \frac{e^2 \hbar}{\pi mc} \frac{\alpha_{ij}(0)}{r^5} \left[ -\frac{1}{8} \delta_{ij} + \frac{25}{8} \hat{x}_i \hat{x}_j \right] - e^2 a_0 \frac{\beta_{ij}(0)}{r^6} \left[ \frac{1}{2} \delta_{ij} + \frac{3}{2} \hat{x}_i \hat{x}_j \right] \right\}.$$

(2.21)

We also introduce $y \equiv E_{10} r / h c$ and the auxiliary functions $f$ and $g$ of the sine and cosine integrals [22],

$$f(y) = Ci(y) \sin y - si(y) \cos y,$$

(2.22)

$$g(y) = -Ci(y) \cos y - si(y) \sin y.$$

(2.23)

Using (2.11) and (2.21) we follow paper I and use parametric differentiations with respect to $t$ of the integral representation of $f(ty)$, with

$$\int_{0}^{\infty} \frac{\sin(tx)}{x+y} dx = f(ty),$$

(2.24)

to complete the integration in (2.20); we find

$$V_T(r) = \tilde{V}_\infty(r) + \frac{2e^4}{\pi mc^2 r^4} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{u} \frac{1}{y^2} \langle 0|x_{1i}|u\rangle \langle u|x_{1j}|0\rangle \times \{ \delta_{ij} d(y) + \hat{x}_i \hat{x}_j p(y) \},$$

(2.25)

where

$$d(y) \equiv f(2y) \left( \frac{1}{2} y^4 - \frac{3}{2} y^2 + \frac{1}{2} \right) + g(2y) (y^3 + y) + \frac{9}{8} y - \frac{1}{4} y^3,$$

(2.26)

and

$$p(y) \equiv f(2y) \left( -\frac{1}{2} y^4 - \frac{1}{2} y^2 + \frac{3}{2} \right) + g(2y) (y^3 + 3y) - \frac{1}{4} y + \frac{1}{4} y^3.$$

(2.27)

In order to evaluate $V_T$ numerically, it will prove convenient to express $\tilde{V}_\infty$ in terms of $y$, include it in the sum over $u$, and write

$$V_T(r) = \sum_{i=1}^{3} \sum_{j=1}^{3} (D_{ij} \delta_{ij} + P_{ij} \hat{x}_i \hat{x}_j),$$

(2.28)
where
\[ D_{ij} \equiv \frac{2e^4}{\pi mc^2 r^4} \sum_u \frac{1}{y^2} \langle 0 | x_{1i} | u \rangle \langle u | x_{1j} | 0 \rangle [d(y) - \frac{1}{4} \pi - \frac{1}{8} y], \tag{2.29} \]
and
\[ P_{ij} \equiv \frac{2e^4}{\pi mc^2 r^4} \sum_u \frac{1}{y^2} \langle 0 | x_{1i} | u \rangle \langle u | x_{1j} | 0 \rangle [p(y) - \frac{3}{4} \pi + \frac{25}{8} y]. \tag{2.30} \]

The expansions of the quantity in \{\ldots\} in Eq. (2.25) are
\[ \{\ldots\} \sim y^{-1} \left( \frac{13}{8} \delta_{ij} + \frac{7}{8} \hat{x}_i \hat{x}_j + \ldots \right), \quad y \sim \infty, \tag{2.31} \]
and
\[ \{\ldots\} \sim \left[ \frac{1}{4} \pi + \frac{1}{8} y - \frac{1}{4} \pi y^2 + \left[ -\frac{2}{3} (\gamma + \ln 2y) + \frac{35}{36} y^3 + \frac{1}{4} \pi y^4 \right] \delta_{ij} \right] + \left[ \frac{3}{4} \pi - \frac{25}{8} y + \frac{5}{8} \pi y^2 + \left[ 2(\gamma + \ln 2y) - \frac{49}{12} y^3 - \frac{1}{4} \pi y^4 \right] \hat{x}_i \hat{x}_j \right], \quad y \sim 0, \tag{2.32} \]
where \( \gamma = 0.577\ldots \) is the Euler constant. In the next section, Sec. III B, we will use these expansions to evaluate the small-\( r \) and large-\( r \) limits of \( V_T \) by completing the sums over \( i \) and \( j \). The small-\( r \) limit, which contains terms of order \( r^{-4}, r^{-3}, \) and \( r^{-2} \), is obtained by substituting Eq. (2.32) into Eq. (2.25) and in Sec. III B below we will give explicit expressions for these terms, and discuss their physical meanings, where possible. The asymptotic limit, which results from the substitution of Eq. (2.31) into Eq. (2.25), can be written as
\[ V_T(r) \sim \sum_{i=1}^{3} \sum_{j=1}^{3} \left[ \frac{e^2 \hbar}{\pi mc} \frac{\alpha_{ij}(0)}{r^5} \left[ -\frac{1}{8} \delta_{ij} + \frac{25}{8} \hat{x}_i \hat{x}_j \right] + \frac{\hbar c \gamma_{ij}(0)}{a_0} \frac{\gamma_{ij}(0)}{r^7} \left[ 13 \delta_{ij} + 7 \hat{x}_i \hat{x}_j \right] \right], \quad r \sim \infty, \tag{2.33} \]
where \( \gamma_{ij} \) is defined in Eq. (2.8). The \( r^{-5} \) term, the asymptotic potential, is the result obtained semi-classically [15], and reduces to the usual form [17] for \( \alpha_{ij}(0) = \alpha(0) \delta_{ij} \).

### III. ENERGY SHIFTS

To obtain the energy shifts for a Rydberg state \( nl \) from the various forms of the effective potentials comprising \( V_T \) obtained above we need to evaluate matrix elements. To do so, we first reduce the sums over \( i \) and \( j \) to geometrical factors, then make contact with the work of Eyler and Pipkin [23], who have developed all of the formalism required to obtain reduced matrix elements, and we then evaluate the potentials using a representation of the electric dipole excitation spectrum of \( H_2^+ \). Matrix elements of the potentials over the vibrational-rotational wave function for the \( H_2^+ \) core and the Rydberg electron wave function follow and yield the desired energy shifts.

#### A. Reduction to geometrical factors

In general, the effective potential expression to be evaluated is composed of a scalar product of two symmetric second rank cartesian tensors, thus,
\[ \Omega = \sum_{i=1}^{3} \sum_{j=1}^{3} \Delta_{ij} T_{ij}, \quad (3.1) \]

where \( \Delta_{ij} \) depends on the orientation of the core, \( R \), and possibly \( r \), and could represent \( \alpha_{ij}, \beta_{ij}, \gamma_{ij}, F_{ij}, D_{ij}, \) or \( P_{ij} \). In general, any symmetric second rank tensor would have six independent elements. However, as applied to the \( H_2^+ \) core, the cylindrical symmetry and the choice of principal axes such that the z-axis coincides with the internuclear axis reduce the number of independent elements of each \( \Delta_{ij} \) to two. By inspection of an equation such as (2.28), we see that \( T_{ij} \) is of the form

\[ T_{ij} = A \delta_{ij} + B \hat{x}_i \hat{x}_j, \quad (3.2) \]

with \( A \) and \( B \) scalar factors that are independent of the core properties, such as \( y \).

In the molecule-fixed frame (fixed with the core) in which electronic the matrix element \( \langle 0| x_{1i}| u \rangle \langle u | x_{1j} | 0 \rangle \) appearing in \( \Delta_{ij} \) is calculated, \( \Delta_{ij} \) can be written

\[ \Delta_{ij} = \begin{pmatrix} \Delta^\perp & 0 & 0 \\ 0 & \Delta^\perp & 0 \\ 0 & 0 & \Delta^\parallel \end{pmatrix}, \quad (3.3) \]

with \( \Delta^\perp \) and \( \Delta^\parallel \) the two independent elements. As in Ref. [15] for the particular case of \( \alpha_{ij} \), it is convenient to work with two different independent elements,

\[ \Delta_s \equiv \frac{1}{3} (2 \Delta^\perp + \Delta^\parallel), \quad \Delta_t \equiv \Delta^\parallel - \Delta^\perp, \quad (3.4) \]

because \( \Delta_s \) and \( \Delta_t \) have simple transformation properties [24]. Eq. (3.4) is not surprising. The coefficients 2 and 1 in \( \Delta_s \) reflect the fact that there are two directions perpendicular to the internuclear axis and one parallel. Thus, since \( \Delta_s = \frac{1}{3} \text{Tr} \Delta_{ij}, \Delta_s \) is a scalar. Further, roughly speaking, with \( b \) a number,

\[ \Delta^\perp = \Delta_{11} = \Delta_{22} = \frac{1}{2} (\Delta_{11} + \Delta_{22}) = \frac{1}{2} b \sin^2 \theta, \quad (3.5) \]

\[ \Delta^\parallel = b \cos^2 \theta, \quad (3.6) \]

so that

\[ \Delta_t = b \left[ \cos^2 \theta - \frac{1}{2} (1 - \cos^2 \theta) \right] = b P_2 (\cos \theta), \quad (3.7) \]

that is, \( \Delta_t \) is proportional to \( Y_{20} \), a component of a symmetric traceless second rank tensor. Note that for \( \Delta^\perp = \Delta^\parallel \equiv \Delta_s \), in which case \( \Delta_{ij} \) has only one independent element, \( \Delta_s = \Delta \) and \( \Delta_t = 0 \). We will now proceed more formally.

\( T_{ij} \) can be decomposed into a linear combination of two irreducible components, one transforming as a scalar, and one transforming as a traceless symmetric tensor, denoted by \( S_{ij} \), as

\[ T_{ij} = (A + \frac{1}{3} B) \delta_{ij} + BS_{ij}, \quad (3.8) \]

where
\[ S_{ij} \equiv \hat{z}_i \hat{z}_j - \frac{1}{2} \delta_{ij}, \]  
\hspace{1cm} (3.9) 

using \( \text{Tr} \hat{z}_i \hat{z}_j = 1 \). We can then write, using (3.5) and (3.6),

\[ \Omega = \sum_{i=1}^{3} \Delta_{ii} T_{ii} = \Delta^\perp (T_{11} + T_{22}) + \Delta^\parallel T_{33}, \]  
\hspace{1cm} (3.10) 

and using (3.8) to replace \( T_{ii} \) we have

\[ \Omega = (A + \frac{1}{3} B)[2\Delta^\perp + \Delta^\parallel] + B[\Delta^\perp (S_{11} + S_{22}) + \Delta^\parallel S_{33}]. \]  
\hspace{1cm} (3.11) 

With the definition of \( S_{ii} \), (3.9), we can write

\[ \Omega = (3A + B)\Delta_\perp + B[\Delta^\perp (\hat{z}_1^2 + \hat{z}_2^2 - \frac{2}{3}) + \Delta^\parallel (\hat{z}_3^2 - \frac{1}{3})] \]  
\hspace{1cm} (3.12) 

and since \( \sum_{i=1}^{3} \hat{z}_i^2 = 1 \) and \( \hat{z}_3^2 = \cos^2 \theta \), we have the final result

\[ \Omega = (3A + B)\Delta_\perp + \frac{2}{3} B \Delta_\parallel P_2(\cos \theta). \]  
\hspace{1cm} (3.13) 

The result for \( \Omega \) obtained in Eq. (3.13) is identical to that worked out by Eyler and Pipkin. [To see that, note that \( P_2(\cos \theta) = C_0^{(2)}(\theta, \phi) \), with \( C_0^{(2)} \) a spherical-harmonic tensor in the notation of Ref. [23] and where \( \theta, \phi \) are the angles of the Rydberg electron relative to the core (in Ref. [23] these were denoted \( \omega, \nu \)).] That \( \Omega \) is \( \phi \) independent is expected due to the cylindrical symmetry of the core charge distribution seen by the Rydberg electron. For example, we can check Eq. (3.13) by seeing that for \( A = 0 \) and \( B = 1 \) it reproduces the result of Ref. [23], the equation above their Eq. (7), for the electric dipole polarization potential expressed in the molecule-fixed frame. We will use relation Eq. (3.13) repeatedly to reduce products of the form of Eq. (3.1). Note that Eyler and Pipkin started with a classically-derived expression for the polarization potential and then obtained expectation values using quantum-mechanical wave functions, while an alternative derivation has been given by Sturctus et al. [20], who used quantum mechanics to derive the polarization potential in second order perturbation theory and also to obtain expectation values. The latter approach has the advantage that it can readily be adapted to obtain higher order “nonadiabatic” potentials.

In Hound’s case (d) the orbital angular momentum vector \( \mathbf{l} \) of the Rydberg electron is space-fixed and it is desirable to transform to the space-fixed frame in obtaining reduced matrix elements. Eyler and Pipkin have carried out the transformation and the angular momentum algebra to obtain reduced matrix elements for \( \Omega \). Since our Eq. (3.13) provides the connection to their molecule-fixed frame expression, we can proceed directly from their Eq. (7) to obtain the final expression for the matrix element of \( \Omega \). Introducing the vibrational quantum number \( v \) and the angular momentum quantum numbers \( N, l, J \), where \( J = |l + N| \) is the total angular momentum less electron and nuclear spin, with \( N \) the core rotational angular momentum, we have

\[ \langle v N n l; J | \Omega | v N n l; J \rangle = \langle n l v N | (3A + B)\Delta_\perp | n l v N \rangle \]
\[ + \frac{2}{3} \langle n l v N | B \Delta_\parallel | n l v N \rangle \langle N, l; J | P_2(\cos \theta) | N, l; J \rangle, \]  
\hspace{1cm} (3.14) 

where \( |n l v N \rangle = |n l \rangle |v N \rangle \), \( |l - N| \leq J \leq |l + N| \), and the diagonal coupling can be expressed using [23]
\[ \langle N, l; J|P_2(\cos \theta)|N, l; J \rangle = \frac{3Y(Y - 1) - 4N(N + 1)l(l + 1)}{2(2N - 1)(2l - 1)(2N + 3)(2l + 3)} \]  

(3.15)

with

\[ Y = N(N + 1) + l(l + 1) - J(J + 1), \]

(3.16)

see also Ref. [20]. (Note that Eyler and Pipkin used the symbols \( R, L, N \), where we have used, respectively, \( N, l, J \).) The selection rules are given in Ref. [23]. We consider only terms diagonal in \( N \); the term \( P_2(\cos \theta) \) can couple states that differ in \( N \) by \( \pm 2 \) for a given \( l \) and \( J \), and such couplings can be treated using perturbation theory, but they are small and we ignore them because their relative effect on the retardation energy shift is expected to be small. For the common case of \( N = 1 \), Eq. (3.15) yields

\[ \langle 1, l; l|P_2(\cos \theta)|1, l; l \rangle = -\frac{1}{5}, \]

(3.17)

and

\[ \langle 1, l; l + 1|P_2(\cos \theta)|1, l; l + 1 \rangle = l/[5(2l + 3)] \]

(3.18)

\[ \langle 1, l; l - 1|P_2(\cos \theta)|1, l; l - 1 \rangle = (l + 1)/[5(2l - 1)], \]

(3.19)

both of which tend to \( \frac{1}{10} \) as \( l \to \infty \).

(An alternative method would be to proceed directly from Eqs. (3.1) and (3.8) to reduced matrix elements by using Ramsey's theorem [25], which suggests itself due to the quadrupolar form of the tensors in Eq. (3.1). The theorem may be used to obtain diagonal matrix elements of second rank symmetric traceless tensors that commute with some angular momentum vector in the same manner as the relevant coordinate vector commutes with the angular momentum vector. Propin [26] applied this method successfully to obtain some energy shifts due to the electron spin-dependent interactions (the so-called magnetic fine structure) for \( \text{H}_2 \).)

**B. Numerical evaluation**

The oscillator strengths, defined to be

\[ f^\parallel_{u0} = \frac{2}{3} E^\parallel_{u0} |\langle u|x|0 \rangle|^2 (e^2 a_0)^{-1}, \]

(3.20)

\[ f^\perp_{u0} = \frac{2}{3} E^\perp_{u0} |\langle u|x|0 \rangle|^2 (e^2 a_0)^{-1}, \]

(3.21)

where \( z = z_{13} \) and \( x = z_{11} \) are, respectively, parallel and perpendicular to the internuclear axis, \( E^\parallel_{u0} \equiv E_u - E_0 \) for \( |u \rangle \) a \( \sigma_u \) state and \( E^\perp_{u0} \equiv E_u - E_0 \) for \( |u \rangle \) a \( \pi_u \) state, obey the Thomas-Reiche-Kuhn sum rule

\[ \sum_u (f^\parallel_{u0} + f^\perp_{u0}) = 1. \]

(3.22)
The $\parallel$ and $\perp$ components of the polarizabilities $\alpha_{ij}$, $\beta_{ij}$, $\gamma_{ij}$ are proportional, respectively, with $n = -2, -3, -4$, to the dimensionless sums

$$ S^\parallel(n) = 3 \sum_u f_{u0}^{\parallel}(E_{u0}/E_H)^n $$

and

$$ S^\perp(n) = \frac{3}{2} \sum_u f_{u0}^{\perp}(E_{u0}/E_H)^n, $$

where $E_H = e^2/a_0$. Thus, for example, we have

$$ \alpha^\parallel(0) = 3a_0^3 \sum_u f_{u0}^{\parallel}/(E_{u0}/E_H)^2 = a_0^3 S^\parallel(-2) $$

and

$$ \alpha^\perp(0) = \frac{3}{2}a_0^3 \sum_u f_{u0}^{\perp}/(E_{u0}/E_H)^2 = a_0^3 S^\perp(-2), $$

and, with $\kappa$ representing $\parallel$ or $\perp$, analogously, $\beta^\kappa = \frac{1}{2}a_0^4 S^\kappa(-3)$ and $\gamma^\kappa = \frac{1}{4}a_0^6 S^\kappa(-4)$, according to our definitions, Eqs. (2.6) and (2.8). Numerical values of the sums (3.23) and (3.24) at various internuclear distances $R$ have been given by Bates [27] and values of $S_s(n)$ with $n = -2, -3$ have been given by Bishop and Cheung [28].

By introducing the oscillator strengths, defined by Eqs. (3.20) and (3.21), we can re-express Eq. (2.25) for $V_T$ in terms of the scalar and tensor components, using Eqs. (3.1)–(3.13) separately for $D_{ij}$ and $P_{ij}$ in Eqs. (2.29) and (2.30). Thus, with $A = 1$, $B = 0$ for $D_{ij}$ and $A = 0$, $B = 1$ for $P_{ij}$ we have

$$ V_T(r, R, \theta) \equiv V_{T,s}(r, R) + V_{T,t}(r, R)P_2(\cos \theta) = [3D_s(r) + P_s(r)] + \frac{3}{2}P_t(r)P_2(\cos \theta), $$

where the $R$-dependence was re-introduced in the notation on the LHS and where $D_s$, $P_s$, and $P_t$ are defined according to Eq. (3.4) and

$$ D^\parallel(r) = \frac{3e^6a_0}{\pi mc^2r^4} \sum_u f_{u0}^{\parallel}d(y) - \frac{1}{4} \pi - \frac{1}{8}y, $$

$$ P^\parallel(r) = \frac{3e^6a_0}{\pi mc^2r^4} \sum_u f_{u0}^{\parallel}p(y) - \frac{3}{4} \pi + \frac{25}{8}y, $$

$$ D^\perp(r) = \frac{3e^6a_0}{2\pi mc^2r^4} \sum_u f_{u0}^{\perp}d(y) - \frac{1}{4} \pi - \frac{1}{8}y, $$

and

$$ P^\perp(r) = \frac{3e^6a_0}{2\pi mc^2r^4} \sum_u f_{u0}^{\perp}p(y) - \frac{3}{4} \pi + \frac{25}{8}y. $$
A convenient way to evaluate the infinite summation-integration $\sum_u$ is to use pseudostates—a set of $M$ pairs of effective transition energies $\tilde{\omega}_i$ and dipole oscillator strengths $g_i$—and we note that a tabulation for $H_2^+$ with $M = 6$, for both parallel and perpendicular transitions and at various values of the internuclear distance, has been published [29]. These will be used in the subsequent evaluations. A comprehensive tabulation of the various polarizabilities as a function of $R$ is beyond the scope of this paper, but in terms of the dimensionless pseudostates, we have, for example,

$$\alpha^\parallel(0) \approx 3a_0^3 \sum_{i=1}^{M} g_i^\parallel/\langle\tilde{\omega}_i^\parallel\rangle^2,$$

$$\alpha^\perp(0) \approx \frac{3}{2}a_0^3 \sum_{i=1}^{M} g_i^\perp/\langle\tilde{\omega}_i^\parallel\rangle^2.$$  

To evaluate Eqs. (3.28)-(3.31) with pseudostates we need only make the replacements $\sum_u \rightarrow \sum_{i=1}^{M}$, $y \equiv E_{u0r}/\hbar c \rightarrow \tilde{\omega}_i r e^2/a_0^2 \hbar c$ and $f_i \rightarrow g_i$, using the $\perp$ or $\parallel$ set of pseudostates as appropriate.

Before we evaluate $V_T$, we give its small-$r$ and large-$r$ forms, obtained as described above in Sec. II D and expressed in terms of the sums Eqs. (3.23) and (3.24) using the definitions of the $s$ and $t$ components in Eq. (3.4). For small $r$ we find

$$V_T(r, R, \theta) \sim \left\{ \frac{a_0^2}{2 r^4} S_s(-1) + \frac{-7a_0^2}{6 r^3} \frac{e^2}{\hbar c} S_s(0) + \frac{a_0^2}{2 r^2} \left( \frac{e^2}{\hbar c} \right)^2 S_s(1) \right\} P_2(\cos \theta) \left( \frac{e^2}{\hbar c} \right)^2 E_H,$$  

(3.34)

where $L_t(0)$ is obtained from the logarithmic sums

$$L^\parallel(0) = 3 \sum_u f_u^\parallel \ln(E_{u0}/E_H)$$

and

$$L^\perp(0) = \frac{3}{2} \sum_u f_u^\perp \ln(E_{u0}/E_H)$$

(3.36)

that have been tabulated for various $R$ in Ref. [29]. Note that because $S_s(0) = 0$, only the logarithmic sum $L_t(0)$ appears in Eq. (3.34). The small-$r$ limit gives $O((e^2/\hbar c)^2)$ and $O((e^2/\hbar c)^3)$ corrections arising, respectively, from the Breit-Pauli orbit-orbit interaction and two-photon exchange (Araki-Sucher) [30,31] terms.

For large $r$ we find,

$$V_T(r, R, \theta) \sim \left\{ \frac{11a_0^6}{4 \pi r^5} \frac{e^2}{\hbar c} S_s(-2) - \frac{3a_0^6}{2 \pi r^5} S_s(-3) + \frac{23a_0^7}{4 \pi r^7} \frac{\hbar c}{e^2} S_s(-4) \right\} P_2(\cos \theta) \left( \frac{e^2}{\hbar c} \right)^2 E_H.$$  

(3.37)
We also find, in agreement with prior derivations for H₂ [20], the Coulombic potential

\[ V_{II}(r, R, \theta) = \left\{ -\frac{a}{2r^4} S_s(-2) + \frac{3a^3}{2r^6} S_s(-3) + \left[ -\frac{a^4}{3r^4} S_s(-2) + \frac{a^5}{2r^6} S_t(-3) \right] P_2(\cos \theta) \right\} E_H. \]  

(3.38)

Note that the \( s \) and \( t \) components of the nonadiabatic, \( 1/r^6 \), terms in Eqs. (3.37) and (3.38) separately cancel, similarly to the spherically symmetric case of Rydberg helium [32].

All of the quantities dependent on \( E_{e0} \) and the oscillator strengths—that is, the \( \parallel \) and \( \perp \) components of the various polarizabilities \( \alpha, \beta, \) and \( \gamma \), the sums \( S(p) \) and \( L(p) \), and the components of \( V_T \)—depend upon the internuclear distance \( R \). We now need to average these core-dependent quantities over the vibrational-rotational wave function of the \( \text{H}_2^+ \) core. To do so, we require the wave function of the vibrational-rotational part of the Hamiltonian, which we determine in the Born-Oppenheimer approximation by numerically integrating using the Numerov-Cooley method the radial Schrödinger equation corresponding to the Hamiltonian

\[ H_{\text{nuc}} = -\left( \frac{\hbar^2}{M_p} \right) \nabla_R^2 + E_0(R) + e^2/R, \]  

(3.39)

where \( E_0(R) \) is the electronic energy and \( M_p \) is the proton mass. The methods are standard and yield a radial vibrational-rotation wave function \( \chi_{vN}(R) \) that satisfies

\[ \int_0^\infty dR \chi_{vN}^2(R) = 1. \]  

(3.40)

For a given quantity \( Q(r; R) \) known at various discrete values of \( R \) we obtain \( Q_{vN}(r) \), the radial matrix element over the vibrational-rotational state, by evaluating the integral

\[ Q_{vN}(r) \equiv \int_0^\infty dR \chi_{vN}^2(R) Q(r; R), \]  

(3.41)

using Simpson’s rule with the function \( Q(r; R) \) interpolated using cubic splines at the points where \( \chi_{vN}(R) \) is known. We used a value \( M_p = 1836.152701 \) and a step size of 0.001\( a_0 \) in generating the wave function. The matrix elements \( S_{vN}^e(p) \) of the sums calculated using the \( M = 6 \) pseudostates of Ref. [29] are given in Table I for \( v = 0, N = 1 \) and can be used to evaluate the small- and large-\( r \) forms of \( V_{T,vN}(r) \) merely by replacing the sums appearing in Eq. (3.34) or Eq. (3.37) by their averages from Table I. The accuracy of the sums could be improved, if necessary, by using a larger value of \( M \), but the \( M = 6 \) pseudostates are sufficient for the present pilot study.

To evaluate the general expression for \( V_T(r, R, \theta) \), defined by Eq. (3.27), we first insert the \( M = 6 \) pseudostates and evaluate the potentials \( V_{T,s}(r, R) \) and \( V_{T,t}(r, R) \) as functions of \( r \) as in Ref. [33], but unlike the potential for He, the potentials are also functions of \( R \). We then carry out as described above the average in Eq. (3.41) for each value of \( r \). In Table II, some results are given for \( V_{T,s,vN} \) and \( V_{T,t,vN} \) for \( v = 0, N = 1 \) and various values of \( r \). The expansion of Eq. (3.27) for small-\( r \), Eq. (3.34), is accurate to better than 0.1% for \( r \leq 5a_0 \), while the expansion for large-\( r \), Eq. (3.37), is accurate to better than 0.1% for \( r \geq 3000a_0 \), and so we have tabulated \( V_T \) from Eq. (3.27) only for the range \( 5 \leq r/a_0 \leq 3000 \). Finally, to obtain the corresponding energy shift, we need to take the matrix element over the Rydberg
electron wave function $|nl\rangle \equiv \psi_{nl}(r)$, which was carried out as described in Ref. [33]. In Table III we give the retardation energy shifts

$$\Delta E_{ret,s}(nlvN) \equiv \langle nl|V_{T,s,vN}(r)|nl\rangle$$  \hspace{1cm} (3.42)

and

$$\Delta E_{ret,t}(nlvN) \equiv \langle nl|V_{T,t,vN}(r)|nl\rangle$$  \hspace{1cm} (3.43)

calculated for the $v = 0, N = 1$ state of $H_2^+$ for various values of $n$ and $l$. Note that for the $t$ component the expectation value Eq. (3.15) of $P_2(\cos \theta)$ was not included in the expression for the energy shift, as discussed below. Various approximations have been made in arriving at the results presented in Table III. For example, $l$ should be large enough that case (d) coupling applies; the corrections become more significant as one goes to lower values of $l$.

C. Prospects for measurement

The most accurate measurements for Rydberg $H_2$ were carried out by Sturrus et al. [14], who measured fine structure transitions for $n = 10$ and $l' - l = 1$ with a $v = 0, N = 1$ core. For each measured transition $|vNLJ\rangle - |vNL'J'\rangle$, where $J - J'$ could be $0, \pm 1$, they defined a "pure electric fine structure (EFS)" interval $E(l, J)$ that represents the measured energy shift in the absence of spin (and exchange) effects, and which could be fit most accurately using the expression

$$E(l, J) = A_0(v, N, n, l) + A_1(v, N, n, l)\langle N, l; J|N \cdot l|N, l; J \rangle$$
$$+ A_2(v, N, n, l)\langle N, l; J|P_2(\cos \theta)|N, l; J \rangle + E^{[2]}_{pol}(l, J),$$  \hspace{1cm} (3.44)

where $A_0$, $A_1$, and $A_2$ represent empirical values for the "structure factors," and where $E^{[2]}_{pol}(l, J)$ is the theoretical "second-order polarization energy," which includes energy shifts arising from off-diagonal couplings. The empirical structure factors are the scalar and tensor coefficients appearing in the energy. [In the theoretical model used by Sturrus et al. $A_1 = 0,$ they also investigated a fit in which this term was omitted and the results were similar to those obtained using Eq. (3.44).]

We shall abbreviate $A_0(0, 1, 0, l)$ as $A_0(l)$ and similarly for $A_2$. The measurements yielded (see Table VIII of Ref. [14]) a value of $A_0(g) - A_0(h)$ with a precision (one-standard-deviation error) of 3.3 MHz, $A_0(h) - A_0(i)$ with a precision of 0.5 MHz, and $A_0(i) - A_0(k)$ with a precision of 0.3 MHz, and values of $A_2(l)$, for $l = g, h, i,$ and $k$, with precisions ranging from 23 to 0.5 MHz. Our predicted $s$ component energy shifts due to retardation, from Table III, would appear in the $A_0$ structure factor and are 0.15, 0.045, and 0.017 MHz, for, respectively, $A_0(g) - A_0(h)$, $A_0(h) - A_0(i)$, and $A_0(i) - A_0(k)$. The predicted $t$ component energy shifts from Table III, which would appear in $A_2$, are 0.24, 0.08, 0.03, and 0.015 MHz, for, respectively, $l = g, h, i,$ and $k$. In each case the shifts are of the order 10 to 100 times smaller than the experimental precision. It might be possible to improve the experimental precision by a factor of 10, and perhaps to the level of 0.01 MHz [14].

In order to isolate the retardation effect one needs to know the energy shift due to the other potentials present (adiabatic and nonadiabatic polarization potentials, potentials due
to permanent multipoles, etc.). From Table VIII of Ref. [14] we see that for $A_0$ the estimated precision of the theoretical determination of these other effects is about 10 to 100 times the experimental precision. For $A_2$ the estimated precision in the theoretical determination is of the order 2 to 5 times the experimental precision, but there is a considerable discrepancy between theory and experiment, of the order 4 to 100 MHz, in the magnitude of $A_2$. To improve upon the theoretical estimates for the other effects will take a considerable effort, perhaps a comprehensive perturbative approach such as that used by Drachman [34] for Rydberg helium, including the calculation of new terms, such as the nonadiabatic potential depending on $\gamma$, Eq. (2.8), which we discussed in Sec. II A above, or a variational basis set approach, such as that used by Drake for Rydberg helium [35].

In our calculation we have neglected the effect of the reduced mass of the core and Rydberg electron, which could be treated by formulating the problem in Jacobi coordinates [14], the Rydberg constant for H$_2$, $R = 109707.4496$ cm$^{-1}$ [36], which would modify slightly the length scale in the radial equation for $\psi_{nl}(r)$ [21], exchange energies [37], relativistic "p$^4$" corrections, second order perturbations [14], magnetic fine structure [38] and hyperfine [39] effects, all of which may need to be understood before a reliable quantitative verification of the retardation potential is achievable.

The final result, Eq. (3.27), could be applied with little modification to obtain an estimate of the retardation energy shifts for other Rydberg molecules with $^2\Sigma^+_g$ cores, providing sets of pseudostates are available. For example, there have been measurements of the $8f$, $9f$, and $10f$ Rydberg states of N$_2$ of which the $8f$ data were used to determine the permanent quadrupole moment and $\alpha_s(0)$ for the $v = 1$ $^2\Sigma^+_g$ N$_2$ core [40] (and references therein for other molecules).

IV. CONCLUSIONS

We have shown that the retardation potential obtained using a semi-classical approach [15] can be extended analogously to the extension obtained for Rydberg He [18]; for He one replaces the dynamic electric polarizability $\alpha(\omega)$ for He$^+$ by $F(\omega)$ for He$^+$, while for H$_2$ one replaces $\alpha_{ij}(\omega)$ for H$_2^+$ by $F_{ij}(\omega)$ for H$_2^+$. The retardation energy shift is an order of magnitude smaller than each of the present theoretical and experimental uncertainties. With some effort, it seems likely that both theoretical and experimental results could be improved to the point at which the retardation shift would be detectable. Apart from the interest in confirming a retardation shift, a knowledge of the shift allows greater accuracy in the determination of the various parameters which characterize the H$_2^+$ core.

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TABLES

TABLE I. Values of the sums $S_{01}^{\parallel}(p)$, $S_{01}^{\perp}(p)$, $L_{01}^{\parallel}(0)$, and $L_{01}^{\perp}(0)$, for the matrix elements over the $v = 0, N = 1$ vibration-rotational wave function calculated using the $M = 6$ pseudostates.

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<th>$S_{01}^{\perp}(p)$</th>
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TABLE II. Values of $V_{T,s,01}(r)$ and $V_{T,l,01}(r)$ in units of $E_H$. Numbers in square brackets represent powers of 10.

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TABLE III. The retardation energy shifts $\Delta E_{\text{ret},x}$, Eq. (3.42), and $\Delta E_{\text{ret},y}$, Eq. (3.43), in MHz, for $v = 0, N = 1$ and various values of $n$ and $l$. Numbers in square brackets represent powers of 10.

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