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Retardation (or Casimir) potential for the Rydberg hydrogen molecule

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The retardation (or Casimir) potential for Rydberg H_2—a hydrogen molecule with one electron in a highly excited, hydrogen-atom-like electronic state and an ${H_2}^+$ 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 a_0 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 *quantitative* 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, dielectric, 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 quite accurate 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 $1s$ 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 heliumlike ions (${}^{12}C^{4+}, {}^{16}O^{6+}, ...,$) have obvious merits, such as the absence of nuclear spin, a one-electron core, hydrogenlike 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 ${H_2}^+$ 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-${H_2}^+$ long-range forces from spectroscopic measurements is achievable. From the theoretical point of view, the ${H_2}^+$ 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 semiclassical theory, we recently derived the exact asymptotic form for the retardation interactions in Rydberg H_2 (the result is applicable also to the case of a Rydberg atom with a P state core; see also Sec. III C below). The result obtained [15] was

$$V(r,\theta) \sim \frac{\hbar e^2}{\pi m c r^5}[\tfrac{11}{4}\alpha_s(0) + \tfrac{25}{12}\alpha_t(0)P_2(\cos\theta)], \quad r \sim \infty, \tag{1.1}$$

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where $\alpha_s(0)$ and $\alpha_t(0)$ are, respectively, the components of the static scalar and tensor electric dipole polarizabilities of the $H_2{}^+$ core, to be defined in detail later, $r = |\mathbf{r}|$ is the distance of the Rydberg electron from the center of mass of the nuclei, and θ 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

$$\alpha_d(k) = \frac{2}{3} e^2 \sum_u \frac{|\langle 0|\mathbf{r}_1|u\rangle|^2 E_{u0}}{E_{u0}^2 - E_k^2}, \qquad (2.1)$$

where the wave function $|0\rangle$ and energy E_0 referred to the $1s$ state hydrogenlike He^+ core electron and the wave function $|u\rangle$ and energy E_u referred to an intermediate p-state, $E_{u0} \equiv E_u - E_0$, $\mathbf{r}_1$ was the position vector of the core electron from the nucleus, and $E_k = \hbar ck$ was the energy of the virtual photon. For Rydberg H_2 the analogous quantity is

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

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 σ_u or π_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 $E_k = \hbar ck$ is again the energy of the virtual photon. (We will use the Born-Oppenheimer approximation for $|0\rangle$ and $|u\rangle$.) Thus, $\alpha_{ij}(k)$ for $H_2{}^+$ is the analog of $\alpha_d(k)$ for He^+. [For $|0\rangle$ in Eq. (2.2) spherically symmetric, $\alpha_{ij}(k)$ reduces to $\alpha_d(k)\delta_{ij}$.]

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 (see Appendix), extended to Rydberg H_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

$$V_{II}(\mathbf{r}) = -e^4 \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{u,v} \langle 0n|x_{1i}x_i r^{-3}|uv\rangle \times \langle uv|x_{1j}x_j r^{-3}|0n\rangle (E_{u0} + E_{vn})^{-1}. \qquad (2.3)$$

The quantities $|0\rangle, |u\rangle, E_{u0}, x_{1i}$, and $r = |\mathbf{r}|$ were defined above, $|n\rangle$ represents the hydrogenlike 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, $E_{vn} \equiv E_v - E_n$, and x_j is a Cartesian component of $\mathbf{r}$.

Expanding the denominator of Eq. (2.3) in powers of E_{vn}/E_{u0}, the first term, $1/E_{u0}$, yields the adiabatic polarization potential

$$V_{\rm pol}(\mathbf{r}) \equiv -\tfrac{1}{2}e^2 \sum_{i=1}^{3}\sum_{j=1}^{3} \alpha_{ij}(0)\hat{x}_i\hat{x}_j/r^4, \qquad (2.4)$$

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

The next term in the denominator expansion, $-E_{vn}/E_{u0}^2$, yields, after some manipulation, the nonadiabatic potential

$$V_{\rm nonad}(\mathbf{r}) \equiv \sum_{i=1}^{3}\sum_{j=1}^{3} \frac{e^2 a_0 \beta_{ij}}{2r^6}(\delta_{ij} + 3\hat{x}_i\hat{x}_j), \qquad (2.5)$$

where

$$\beta_{ij} \equiv e^4 \sum_u \frac{\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle}{E_{u0}^2}. \qquad (2.6)$$

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

$$\sum_v \langle n|x_i r^{-3}|v\rangle\langle v|x_j r^{-3}|n\rangle E_{vn} = \tfrac{1}{2}\langle n|x_i r^{-3}[T_2, x_j r^{-3}] + [x_i r^{-3}, T_2]x_j r^{-3}|n\rangle, \qquad (2.7)$$

where $T_2 = p^2/2m$ is the kinetic energy of the Rydberg electron, and use the property $\beta_{ij} = \beta_{ji}$. 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 β_{ij} is the analog of $\beta_{\rm nonad}$ for helium [17] and reduces to $\beta_{\rm nonad}\delta_{ij}$ for $|0\rangle$ spherically symmetric. There unfortunately exist many different definitions of $\beta_{\rm nonad}$ for atoms, and the same is true for β_{ij}; we note that the definition of β_{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. (3.39) below.

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

$$\gamma_{ij}(0) \equiv \frac{1}{8}\left(\frac{\hbar}{mc}\right)^2 \left.\frac{d^2\alpha_{ij}(k)}{dk^2}\right|_{k=0}, \qquad (2.8)$$

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 $1/r^7$ [14,21]. We hope to present an expression for this potential in a future paper.

For a hydrogenlike ion (core) $\alpha_d(0) = \frac{9}{2}Z^{-4}a_0^3$, $\beta_{\rm nonad}(0) = \frac{43}{8}Z^{-6}a_0^4$, 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

$$V_{IT}(\mathbf{r}) = \frac{2e^2\hbar}{\pi m c r^3} \sum_{i=1}^{3}\sum_{j=1}^{3} \int_0^\infty k F_{ij}(k) J_{ij}(kr)\, dk\ , \qquad (2.9)$$

with

$$J_{ij}(kr) = \delta_{ij}[-\tfrac{1}{3}j_0(kr) + \tfrac{1}{6}j_2(kr)] + 3\hat{x}_i\hat{x}_j[\tfrac{1}{3}j_0(kr) + \tfrac{1}{6}j_2(kr)], \qquad (2.10)$$

where j_0 and j_2 are spherical Bessel functions and

$$F_{ij}(k) = 2e^2 \sum_u \frac{\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle}{E_{u0} + E_k}. \qquad (2.11)$$

C. The evaluation of V_{TT}

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

$$V_{TT}(\mathbf{r}) = \frac{2}{9}\frac{e^2}{\pi^2 m c^2} \lim_{\mu\to 0} \sum_{i=1}^{3}\sum_{j=1}^{3} \int_0^\infty dk k^3 e^{-\mu k} \times H_{ij}(k) G_{ij}(kr)\ , \qquad (2.12)$$

with

$$H_{ij}(k) = 2e^2 \sum_u \frac{\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle E_{u0}}{E_{u0} + E_k}\ , \qquad (2.13)$$

and[1]

$$G_{ij}(kr) = \frac{1}{k}\mathrm{P}\int_0^\infty dk' \frac{k'^2}{k^2 - k'^2}\{4j_0(kr)j_0(k'r)\delta_{ij} - 2[j_0(kr)j_2(k'r) + j_2(kr)j_0(k'r)](\delta_{ij} - 3\hat{x}_i\hat{x}_j) + j_2(kr)j_2(k'r)(\delta_{ij} + 3\hat{x}_i\hat{x}_j)\}, \qquad (2.14)$$

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

$$G_{ij}(s) = \tfrac{3}{2}\pi(\{[-2j_0(s) + j_2(s)]s^{-3} - 3I_d(s)\}\delta_{ij} + \{[2j_0(s) + j_2(s)]s^{-3} - I_p(s)\}3\hat{x}_i\hat{x}_j), \qquad (2.15)$$

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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.

where

$$I_d(s) = \tfrac{1}{2}\sin(2s)(s^{-2} - 3s^{-4} + s^{-6}) + \cos(2s)(s^{-3} - s^{-5}), \tag{2.16}$$

and

$$I_p(s) = \tfrac{1}{2}\sin(2s)(-s^{-2} - s^{-4} + 3s^{-6}) + \cos(2s)(-s^{-3} - 3s^{-5}). \tag{2.17}$$

Using the identity

$$E_{u0}/(E_{u0} + E_k) = 1 - [E_k/(E_{u0} + E_k)] \tag{2.18}$$

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

$$\begin{aligned} V_{TT}(\mathbf{r}) = {} & \frac{-2e^2\hbar}{\pi mc} \lim_{\mu\to 0} \sum_{i=1}^{3}\sum_{j=1}^{3} \int_0^\infty dk k^4 e^{-\mu k} F_{ij}(k) \\ & \times\{-\tfrac{1}{2}[I_d(kr)\delta_{ij} + I_p(kr)\hat{x}_i\hat{x}_j] \\ & + (1/k^3r^3)J_{ij}(kr)\}. \end{aligned} \tag{2.19}$$

D. The sum V_T of V_{IT} and V_{TT}

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

$$\begin{aligned} V_T(\mathbf{r}) & \equiv V_{IT}(\mathbf{r}) + V_{TT}(\mathbf{r}) \\ & = \frac{e^2\hbar}{mc} \lim_{\mu\to 0} \sum_{i=1}^{3}\sum_{j=1}^{3} \int_0^\infty dk k^4 e^{-\mu k} F_{ij}(k) \\ & \quad \times[\delta_{ij} I_d(kr) + \hat{x}_i\hat{x}_j I_p(kr)]. \end{aligned} \tag{2.20}$$

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 semiclassical argument. We will return to this point in the last section.

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

$$\begin{aligned} \tilde{V}_\infty(\mathbf{r}) \equiv \sum_{i=1}^{3}\sum_{j=1}^{3} \bigg\{ & \frac{e^2\hbar}{\pi mc} \frac{\alpha_{ij}(0)}{r^5}[-\tfrac{1}{8}\delta_{ij} + \tfrac{25}{8}\hat{x}_i\hat{x}_j] \\ & - e^2 a_0 \frac{\beta_{ij}(0)}{r^6}[\tfrac{1}{2}\delta_{ij} + \tfrac{3}{2}\hat{x}_i\hat{x}_j] \bigg\}. \end{aligned} \tag{2.21}$$

We also introduce

$$y \equiv E_{u0} r/\hbar c \tag{2.22}$$

and the auxiliary functions f and g of the sine and cosine integrals [22],

$$f(y) = \mathrm{Ci}(y)\sin y - \mathrm{si}(y)\cos y, \tag{2.23}$$

$$g(y) = -\mathrm{Ci}(y)\cos y - \mathrm{si}(y)\sin y. \tag{2.24}$$

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

$$\int_0^\infty \frac{\sin(tx)}{x+y} dx = f(ty), \tag{2.25}$$

to complete the integration in (2.20); we find

$$\begin{aligned} V_T(\mathbf{r}) = {} & \tilde{V}_\infty(\mathbf{r}) \\ & + \frac{2e^4}{\pi mc^2 r^4} \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_u \frac{1}{y^2}\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle \\ & \times\{\delta_{ij} d(y) + \hat{x}_i\hat{x}_j p(y)\}, \end{aligned} \tag{2.26}$$

where

$$\begin{aligned} d(y) \equiv {} & f(2y)(\tfrac{1}{2}y^4 - \tfrac{3}{2}y^2 + \tfrac{1}{2}) \\ & + g(2y)(-y^3 + y) + \tfrac{9}{8}y - \tfrac{1}{4}y^3 \end{aligned} \tag{2.27}$$

and

$$\begin{aligned} p(y) \equiv {} & f(2y)(-\tfrac{1}{2}y^4 - \tfrac{1}{2}y^2 + \tfrac{3}{2}) \\ & + g(2y)(y^3 + 3y) - \tfrac{1}{8}y + \tfrac{1}{4}y^3. \end{aligned} \tag{2.28}$$

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

$$V_T(\mathbf{r}) \equiv \sum_{i=1}^{3}\sum_{j=1}^{3}(D_{ij}\delta_{ij} + P_{ij}\hat{x}_i\hat{x}_j), \tag{2.29}$$

where

$$D_{ij} \equiv \frac{2e^4}{\pi mc^2 r^4} \sum_u \frac{1}{y^2}\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle[d(y) - \tfrac{1}{4}\pi - \tfrac{1}{8}y], \tag{2.30}$$

and

$$P_{ij} \equiv \frac{2e^4}{\pi mc^2 r^4} \sum_u \frac{1}{y^2}\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle[p(y) - \tfrac{3}{4}\pi + \tfrac{25}{8}y]. \tag{2.31}$$

The expansions of the quantity in $\{\cdots\}$ in Eq. (2.26) are

$$\{\cdots\} \sim y^{-1}(\tfrac{13}{8}\delta_{ij} + \tfrac{7}{8}\hat{x}_i\hat{x}_j + \cdots), \qquad y \sim \infty, \tag{2.32}$$

and

$$\begin{aligned} \{\cdots\} \sim {} & \{\tfrac{1}{4}\pi + \tfrac{1}{8}y - \tfrac{1}{4}\pi y^2 \\ & + [-\tfrac{2}{3}(\gamma + \ln 2y) + \tfrac{35}{36}]y^3 + \tfrac{1}{4}\pi y^4\}\delta_{ij} \\ & + \{\tfrac{3}{4}\pi - \tfrac{25}{8}y + \tfrac{5}{4}\pi y^2 \\ & + [2(\gamma + \ln 2y) - \tfrac{49}{12}]y^3 - \tfrac{1}{4}\pi y^4\}\hat{x}_i\hat{x}_j, \qquad y \sim 0, \end{aligned} \tag{2.33}$$

where $\gamma = 0.577...$ 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. (2.33) into Eq. (2.26) 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. (2.32) into Eq. (2.26), can be written as

$$V_T(\mathbf{r}) \sim \sum_{i=1}^{3}\sum_{j=1}^{3}\left[\frac{e^2\hbar}{\pi mc}\frac{\alpha_{ij}(0)}{r^5}[-\tfrac{1}{8}\delta_{ij}+\tfrac{25}{8}\hat{x}_i\hat{x}_j] + \frac{\hbar c}{a_0}\frac{\gamma_{ij}(0)}{r^7}[13\delta_{ij}+7\hat{x}_i\hat{x}_j]\right], \qquad r\sim\infty, \tag{2.34}$$

where γ_{ij} is formally defined in Eq. (2.8). The r^{-5} term, the asymptotic potential, is the result obtained semiclassically [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,

$$\Omega = \sum_{i=1}^{3}\sum_{j=1}^{3}\Delta_{ij}T_{ij}, \tag{3.1}$$

where Δ_{ij} depends on the orientation of the core, R, and possibly r, and could represent α_{ij}, β_{ij}, γ_{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 Δ_{ij} to two. By inspection of an equation such as (2.29), we see that T_{ij} is of the form

$$T_{ij} = A\delta_{ij} + B\hat{x}_i\hat{x}_j, \tag{3.2}$$

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 the electronic matrix element $\langle 0|x_{1i}|u\rangle\langle u|x_{1j}|0\rangle$ appearing in Δ_{ij} is calculated, Δ_{ij} can be written in the form

$$\Delta_{ij} = \begin{pmatrix} \Delta^{\perp} & 0 & 0 \\ 0 & \Delta^{\perp} & 0 \\ 0 & 0 & \Delta^{\parallel} \end{pmatrix}, \tag{3.3}$$

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

$$\Delta_s \equiv \tfrac{1}{3}(2\Delta^{\perp}+\Delta^{\parallel}), \quad \Delta_t \equiv \Delta^{\parallel}-\Delta^{\perp}, \tag{3.4}$$

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

$$\Delta^{\perp} = \Delta_{11} = \Delta_{22} = \tfrac{1}{2}(\Delta_{11}+\Delta_{22}) = \tfrac{1}{2}b\sin^2\theta, \tag{3.5}$$

and

$$\Delta^{\parallel} = b\cos^2\theta, \tag{3.6}$$

so that

$$\Delta_s = \tfrac{1}{3}b, \quad \Delta_t = b[\cos^2\theta - \tfrac{1}{2}(1-\cos^2\theta)] = bP_2(\cos\theta), \tag{3.7}$$

that is, Δ_t is proportional to Y_{20}, a component of a symmetric traceless second-rank tensor. Note that for $\Delta^{\perp} = \Delta^{\parallel} \equiv \Delta$, in which case $\cos^2\theta = \frac{1}{2}$, Δ_{ij} has only one independent element, $\Delta_s = \Delta$. (Δ_t then vanishes.) 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

$$T_{ij} = (A+\tfrac{1}{3}B)\delta_{ij} + BS_{ij}, \tag{3.8}$$

where

$$S_{ij} \equiv \hat{x}_i\hat{x}_j - \tfrac{1}{3}\delta_{ij}, \tag{3.9}$$

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

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

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

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

With (3.4) and the definition of S_{ii}, (3.9), we can write

$$\Omega = (3A+B)\Delta_s + B[\Delta^{\perp}(\hat{x}_1^2+\hat{x}_2^2-\tfrac{2}{3}) + \Delta^{\parallel}(\hat{x}_3^2-\tfrac{1}{3})]\,, \tag{3.12}$$

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

$$\Omega = (3A + B)\Delta_s + \tfrac{2}{3}B\Delta_t P_2(\cos\theta). \tag{3.13}$$

The result for Ω 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 θ,ϕ are the angles of the Rydberg electron relative to the core (in Ref. [23] these were denoted ω,ν).] That Ω is ϕ 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 Sturrus *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 Hund's case (d) the orbital angular momentum vector **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 Ω. 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 Ω. Introducing the vibrational quantum number v and the angular momentum quantum numbers N, l, J, where $J = |\mathbf{l} + \mathbf{N}|$ is the total angular momentum less electron and nuclear spin, with $\mathbf{N}$ the core rotational angular momentum, we have

$$\begin{aligned}\langle vNnl;J|\Omega|vNnl;J\rangle = {}& \langle nlvN|(3A + B)\Delta_s|nlvN\rangle \\ &+ \tfrac{2}{3}\langle nlvN|B\Delta_t|nlvN\rangle \\ &\times\langle N,l;J|P_2(\cos\theta)|N,l;J\rangle,\end{aligned} \tag{3.14}$$

where $|nlvN\rangle = |nl\rangle|vN\rangle$, $|l - N| \le J \le |l + N|$, and the diagonal coupling can be expressed using [23]

$$\langle N,l;J|P_2(\cos\theta)|N,l;J\rangle$$

$$= \frac{3Y(Y-1) - 4N(N+1)l(l+1)}{2(2N-1)(2l-1)(2N+3)(2l+3)}, \tag{3.15}$$

with

$$Y = N(N+1) + l(l+1) - J(J+1), \tag{3.16}$$

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 also couple states that differ in N by ±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

$$\langle 1,l;l|P_2(\cos\theta)|1,l;l\rangle = -\tfrac{1}{5}, \tag{3.17}$$

and

$$\langle 1,l;l+1|P_2(\cos\theta)|1,l;l+1\rangle = l/[5(2l+3)], \tag{3.18}$$

$$\langle 1,l;l-1|P_2(\cos\theta)|1,l;l-1\rangle = (l+1)/[5(2l-1)], \tag{3.19}$$

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 a second-rank symmetric traceless tensor constructed from a vector that commutes 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 H_2.]

B. Numerical evaluation

The oscillator strengths, defined to be

$$f_{u0}^{\parallel} = \tfrac{2}{3}E_{u0}^{\parallel}|\langle u|z|0\rangle|^2(e^2a_0)^{-1}, \tag{3.20}$$

$$f_{u0}^{\perp} = \tfrac{4}{3}E_{u0}^{\perp}|\langle u|x|0\rangle|^2(e^2a_0)^{-1}, \tag{3.21}$$

where $z = x_{13}$ and $x = x_{11}$ are, respectively, parallel and perpendicular to the internuclear axis, $E_{u0}^{\parallel} \equiv E_{u\parallel} - E_0$ for $|u\rangle$ a σ_u state and $E_{u0}^{\perp} \equiv E_{u\perp} - E_0$ for $|u\rangle$ a π_u state, obey the Thomas-Reiche-Kuhn sum rule

$$\sum_{u\parallel} f_{u0}^{\parallel} + \sum_{u\perp} f_{u0}^{\perp} = 1. \tag{3.22}$$

Since the x, y, and z components give the same value, despite the fact that the ground state is not spherically symmetric, we can decompose Eq. (3.22) into

$$\sum_{u\parallel} f_{u0}^{\parallel} = \tfrac{1}{3}, \quad \sum_{u\perp} f_{u0}^{\perp} = \tfrac{2}{3}. \tag{3.23}$$

The $\parallel$ and $\perp$ components of the polarizabilities α_{ij}, β_{ij}, γ_{ij} are proportional, respectively, with $n = -2, -3, -4$, to the dimensionless sums

$$S^{\parallel}(n) = 3\sum_{u\parallel} f_{u0}^{\parallel}(E_{u0}^{\parallel}/E_H)^n, \tag{3.24}$$

and

$$S^{\perp}(n) = \tfrac{3}{2}\sum_{u\perp} f_{u0}^{\perp}(E_{u0}^{\perp}/E_H)^n, \qquad (3.25)$$

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

$$\alpha^{\parallel}(0) = 3a_0^3 \sum_{u\parallel} f_{u0}^{\parallel}/(E_{u0}^{\parallel}/E_H)^2 = a_0^3 S^{\parallel}(-2) \qquad (3.26)$$

and

$$\alpha^{\perp}(0) = \tfrac{3}{2}a_0^3 \sum_{u\perp} f_{u0}^{\perp}/(E_{u0}^{\perp}/E_H)^2 = a_0^3 S^{\perp}(-2), \qquad (3.27)$$

and, with κ 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 (3.24) and (3.25) at various internuclear distances R have been given by Bates [27] and values of $S_s(n) = \frac{1}{3}[2S^{\perp}(n) + S^{\parallel}(n)]$ 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 reexpress Eq. (2.26) 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. (2.30) and (2.31). Thus, with $A = 1$, $B = 0$ for D_{ij} and $A = 0$, $B = 1$ for P_{ij} we have

$$\begin{aligned} V_T(r,R,\theta) &\equiv V_{T,s}(r,R) + V_{T,t}(r,R)P_2(\cos\theta) \\ &= [3D_s(r) + P_s(r)] + \tfrac{2}{3}P_t(r)P_2(\cos\theta), \end{aligned} \qquad (3.28)$$

where the R dependence was reintroduced in the notation on the left hand side and where D_s, P_s, and P_t are defined according to Eq. (3.4) and

$$D^{\parallel}(r) = \frac{3e^6 a_0}{\pi m c^2 r^4} \sum_{u\parallel} \frac{f_{u0}^{\parallel}}{E_{u0} y^2}[d(y) - \tfrac{1}{4}\pi - \tfrac{1}{8}y], \qquad (3.29)$$

$$P^{\parallel}(r) = \frac{3e^6 a_0}{\pi m c^2 r^4} \sum_{u\parallel} \frac{f_{u0}^{\parallel}}{E_{u0} y^2}[p(y) - \tfrac{3}{4}\pi + \tfrac{25}{8}y], \qquad (3.30)$$

$$D^{\perp}(r) = \frac{3e^6 a_0}{2\pi m c^2 r^4} \sum_{u\perp} \frac{f_{u0}^{\perp}}{E_{u0} y^2}[d(y) - \tfrac{1}{4}\pi - \tfrac{1}{8}y], \qquad (3.31)$$

and

$$P^{\perp}(r) = \frac{3e^6 a_0}{2\pi m c^2 r^4} \sum_{u\perp} \frac{f_{u0}^{\perp}}{E_{u0} y^2}[p(y) - \tfrac{3}{4}\pi + \tfrac{25}{8}y]. \qquad (3.32)$$

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,

$$\alpha^{\parallel}(0) \approx 3a_0^3 \sum_{i=1}^{M} g_i^{\parallel}/(\tilde{\omega}_i^{\parallel})^2, \qquad (3.33)$$

$$\alpha^{\perp}(0) \approx \tfrac{3}{2}a_0^3 \sum_{i=1}^{M} g_i^{\perp}/(\tilde{\omega}_i^{\perp})^2. \qquad (3.34)$$

To evaluate Eqs. (3.29)–(3.32) with pseudostates we need only make the replacements $\sum_u \to \sum_{i=1}^{M}$, $y \equiv E_{u0}r/\hbar c \to \tilde{\omega}_i r e^2/a_0\hbar c$ and $f_i \to g_i$, 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. (3.24) and (3.25) using the definitions of the s and t components in Eq. (3.4). For r small but greater than a few a_0 we find

$$\begin{aligned} V_T(r,R,\theta) \sim \Bigg\{ &\frac{a_0^4}{2r^4}S_s(-1) + \frac{-7a_0^3}{6\pi r^3}\frac{e^2}{\hbar c}S_s(0) + \frac{a_0^2}{2r^2}\left(\frac{e^2}{\hbar c}\right)^2 S_s(1) \\ &+ \left[\frac{5a_0^4}{6r^4}S_t(-1) + \frac{4a_0^3}{3\pi r^3}\frac{e^2}{\hbar c}L_t(0) - \frac{a_0^2}{6r^2}\left(\frac{e^2}{\hbar c}\right)^2 S_t(1)\right]P_2(\cos\theta)\Bigg\}\left(\frac{e^2}{\hbar c}\right)^2 E_H, \end{aligned} \qquad (3.35)$$

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

$$L^{\parallel}(0) = 3\sum_{u\parallel} f_{u0}^{\parallel}\ln(E_{u0}/E_H) \qquad (3.36)$$

and

$$L^{\perp}(0) = \tfrac{3}{2}\sum_{u\perp} f_{u0}^{\perp}\ln(E_{u0}/E_H) \qquad (3.37)$$

that have been tabulated for various R in Ref. [29]. Note that because $S_t(0) = 0$, only the logarithmic sum $L_t(0)$ appears in Eq. (3.35). 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,

$$V_T(r,R,\theta) \sim \left\{ \frac{11a_0^5}{4\pi r^5}\frac{e^2}{\hbar c}S_s(-2) - \frac{3a_0^6}{2r^6}S_s(-3) + \frac{23a_0^7}{4\pi r^7}\frac{\hbar c}{e^2}S_s(-4) + \left[\frac{25a_0^5}{12\pi r^5}\frac{e^2}{\hbar c}S_t(-2) - \frac{a_0^6}{2r^6}S_t(-3) + \frac{7a_0^7}{12\pi r^7}\frac{\hbar c}{e^2}S_t(-4) \right] P_2(\cos\theta) \right\} E_H . \quad (3.38)$$

We also find, in agreement with prior derivations for H_2 [20], the Coulombic potential

$$V_{II}(r,R,\theta) = \left\{ -\frac{a_0^4}{2r^4}S_s(-2) + \frac{3a_0^6}{2r^6}S_s(-3) + \left[-\frac{a_0^4}{3r^4}S_t(-2) + \frac{a_0^6}{2r^6}S_t(-3) \right] P_2(\cos\theta) \right\} E_H . \quad (3.39)$$

Note that the s and t components of the nonadiabatic, $1/r^6$, terms in Eqs. (3.38) and (3.39) separately cancel, similarly to the spherically symmetric case of Rydberg helium [32]. (See Appendix.)

All of the quantities dependent on E_{u0} and the oscillator strengths—that is, the $\|$ and $\perp$ components of the various polarizabilities α, β, and γ, 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 ${H_2}^+$ 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

$$H_{\text{nuc}} = -(\hbar^2/M_p)\nabla_R^2 + E_0(R) + e^2/R, \quad (3.40)$$

where $E_0(R)$ is the electronic energy and the reduced mass is $\frac{1}{2}M_p$, with M_p the proton mass. The methods are standard and yield a radial vibrational-rotation wave function $\chi_{vN}(R)$ that satisfies

$$\int_0^\infty dR\, \chi_{vN}^2(R) = 1. \quad (3.41)$$

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

$$Q_{vN}(r) \equiv \int_0^\infty dR\, \chi_{vN}^2(R) Q(r;R), \quad (3.42)$$

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 $M_p = 1\,836.1527$ and a step size of $0.001a_0$ in generating the wave function. The matrix elements $S_{vN}^{\kappa}(p)$ 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. (3.35) or Eq. (3.38) 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, an indication of which are the values of $S_{01}^{\|}(0) = 0.9899$ and $S_{01}^{\perp}(0) = 0.9959$ from Table I; each would be unity if the calculation were exact.

To evaluate the general expression for $V_T(r,R,\theta)$, defined by Eq. (3.28), 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. (3.42) 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. (3.28) for small-r, Eq. (3.35), is accurate to better than 0.1% for $r \leq 5a_0$, while the expansion for large r, Eq. (3.38), is accurate to better than 0.1% for $r \geq 3000a_0$, and so we have tabulated V_T from Eq. (3.28) only for the range $5 \leq r/a_0 \leq 3000$. The near equality of $V_{T,s,01}$ and $V_{T,t,01}$ over the range of R given in Table II appears to be fortuitous. It arises because the s and t coefficients are numerically almost equal for the leading r^{-4} potentials of the small-r expansion *and* for the leading r^{-5} potentials of the large-r expansion. Finally, to obtain the corresponding energy shift, we need to take the matrix element over the Rydberg electron wave function $|nl\rangle \equiv \psi_{nl}(\mathbf{r})$, which was carried out as described in Ref. [33]. In Table III, we give the retardation energy shifts

$$\Delta E_{\text{ret},s}(nlvN) \equiv \langle nl|V_{T,s,vN}(r)|nl\rangle \quad (3.43)$$

and

$$\Delta E_{\text{ret},t}(nlvN) \equiv \langle nl|V_{T,t,vN}(r)|nl\rangle , \quad (3.44)$$

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

TABLE I. Values of the sums $S_{01}^{\|}(p)$, $S_{01}^{\perp}(p)$, $L_{01}^{\|}(0)$, 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.

p	$S_{01}^{\|}(p)$	$S_{01}^{\perp}(p)$
-4	46.01	3.971
-3	15.09	2.667
-2	5.834	1.833
-1	2.337	1.307
0	0.9899	0.9959
1	0.5585	0.8548
	$L_{01}^{\|}(0)$	$L_{01}^{\perp}(0)$
	-0.7918	-0.2237

TABLE II. Values of $V_{T,s,01}(r)$ and $V_{T,t,01}(r)$ in units of E_H. Numbers in square brackets represent powers of 10.

r/a_0	$V_{T,s,01}(r)$	$V_{T,t,01}(r)$
5	6.920[-8]	7.235[-8]
6	3.327[-8]	3.482[-8]
7	1.790[-8]	1.876[-8]
8	1.046[-8]	1.098[-8]
9	6.512[-9]	6.838[-9]
10	4.260[-9]	4.478[-9]
20	2.587[-10]	2.744[-10]
30	4.973[-11]	5.315[-11]
40	1.534[-11]	1.650[-11]
50	6.131[-12]	6.630[-12]
60	2.888[-12]	3.138[-12]
70	1.524[-12]	1.663[-12]
80	8.744[-13]	9.571[-13]
90	5.346[-13]	5.869[-13]
100	3.437[-13]	3.783[-13]
120	1.595[-13]	1.762[-13]
140	8.298[-14]	9.199[-14]
160	4.698[-14]	5.220[-14]
180	2.837[-14]	3.157[-14]
200	1.803[-14]	2.008[-14]
300	3.089[-15]	3.441[-15]
400	8.657[-16]	9.597[-16]
500	3.187[-16]	3.511[-16]
600	1.397[-16]	1.529[-16]
700	6.913[-17]	7.515[-17]
800	3.743[-17]	4.043[-17]
900	2.171[-17]	2.331[-17]
1000	1.331[-17]	1.421[-17]
1400	2.742[-18]	2.874[-18]
2000	5.020[-19]	5.160[-19]
3000	7.103[-20]	7.162[-20]

TABLE III. The retardation energy shifts $\Delta E_{\text{ret},s}$, Eq. (3.43), and $\Delta E_{\text{ret},t}$, Eq. (3.44), in MHz, for $v = 0, N = 1$ and various values of n and l. Numbers in square brackets represent powers of 10.

n	l	$\Delta E_{\text{ret},s}$	$\Delta E_{\text{ret},t}$	n	l	$\Delta E_{\text{ret},s}$	$\Delta E_{\text{ret},t}$
14	13	1.68[-4]	1.87[-4]	11	10	1.40[-3]	1.54[-3]
	12	2.80[-4]	3.10[-4]		9	2.63[-3]	2.88[-3]
	11	4.73[-4]	5.21[-4]		8	5.13[-3]	5.56[-3]
	10	8.19[-4]	8.97[-4]		7	1.06[-2]	1.14[-2]
	9	1.47[-3]	1.60[-3]		6	2.34[-2]	2.50[-2]
	8	2.76[-3]	2.98[-3]		5	5.82[-2]	6.18[-2]
	7	5.52[-3]	5.92[-3]		4	1.71[-1]	1.80[-1]
	6	1.20[-2]	1.28[-2]		3	6.51[-1]	6.83[-1]
	5	2.93[-2]	3.10[-2]	10	9	3.22[-3]	3.52[-3]
	4	8.47[-2]	8.92[-2]		8	6.43[-3]	6.98[-3]
	3	3.20[-1]	3.36[-1]		7	1.35[-2]	1.45[-2]
13	12	3.23[-4]	3.58[-4]		6	3.03[-2]	3.24[-2]
	11	5.57[-4]	6.14[-4]		5	7.59[-2]	8.06[-2]
	10	9.78[-4]	1.07[-3]		4	2.24[-1]	2.36[-1]
	9	1.77[-3]	1.93[-3]		3	8.60[-1]	9.02[-1]
	8	3.36[-3]	3.64[-3]	9	8	8.06[-3]	8.77[-3]
	7	6.76[-3]	7.27[-3]		7	1.73[-2]	1.87[-2]
	6	1.48[-2]	1.58[-2]		6	3.98[-2]	4.26[-2]
	5	3.62[-2]	3.84[-2]		5	1.01[-1]	1.08[-1]
	4	1.05[-1]	1.11[-1]		4	3.02[-1]	3.19[-1]
	3	3.98[-1]	4.18[-1]		3	1.17	1.23
12	11	6.53[-4]	7.22[-4]	8	7	2.25[-2]	2.43[-2]
	10	1.17[-3]	1.29[-3]		6	5.33[-2]	5.70[-2]
	9	2.16[-3]	2.35[-3]		5	1.38[-1]	1.47[-1]
	8	4.13[-3]	4.47[-3]		4	4.20[-1]	4.43[-1]
	7	8.39[-3]	9.02[-3]		3	1.64	1.72
	6	1.85[-2]	1.97[-2]	7	6	7.20[-2]	7.73[-2]
	5	4.55[-2]	4.83[-2]		5	1.94[-1]	2.07[-1]
	4	1.33[-1]	1.40[-1]		4	6.03[-1]	6.37[-1]
	3	5.04[-1]	5.29[-1]		3	2.40	2.51

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 $|vNnlJ\rangle$–$|vNnl'J'\rangle$, 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

$$\begin{aligned} E(l,J) = {} & A_0(v,N,n,l) \\ & + A_1(v,N,n,l)\langle N,l;J|\mathbf{N}\cdot\mathbf{l}|N,l;J\rangle \\ & + A_2(v,N,n,l)\langle N,l;J|P_2(\cos\theta)|N,l;J\rangle \\ & + E^{[2]}_{\text{pol}}(l,J), \end{aligned} \tag{3.45}$$

where A_0, A_1, and A_2 represent empirical values for the "structure factors," and where $E^{[2]}_{\text{pol}}(l, J)$ 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. [Sturrus *et al.* also investigated a fit in which the A_1 term was omitted and the results were similar to those obtained using Eq. (3.45).]

We shall abbreviate $A_0(0,1,10,l)$ 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. The magnitudes of these scalar and tensor shifts are of the order of the measured fine-structure energies appropriately averaged over the spin values (see Table VII of Ref. [14]). Because the coefficients A_0, A_1, and A_2 in Eq. (3.45) have to be fitted to the fine-structure energies, and because the present theoretical values of $E^{[2]}_{\rm pol}$, which also appears in Eq. (3.45), are not yet sufficiently well known, it is not now possible to confirm the Casimir shifts. It might be possible to improve the experimental precision by a factor of 10, and perhaps to the level of 0.01 MHz [14].

Further, 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 10–100 times the experimental precision. For A_2 the estimated precision in the theoretical determination is of the order 2–5 times the experimental precision, but there is a considerable discrepancy between theory and experiment, of the order 4–100 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 terms, such as the nonadiabatic potential depending on γ, 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]. We note that while there is no t component energy shift for $N = 0$ for Rydberg H_2, the s component shift is still present and the corresponding level structure is similar to that of Rydberg helium.

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, $\mathcal{R} = 109\,707.4496$ cm^{-1} [36], which would modify slightly the length scale in the radial equation for $\psi_{nl}(\mathbf{r})$ [21], exchange energies [37], relativistic "p^4" corrections, second-order perturbations [14], magnetic fine structure [38], and hyperfine effects [39], all of which may need to be understood before a truly reliable quantitative verification of the retardation potential is achievable.

The final result, Eq. (3.28), 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). It may be possible to extend the present approach to a Rydberg atom for which the core consists of a relatively inert set of closed shells plus a p (or d, or $f,\ldots$) electron. (A prototype would be a Rydberg carbon atom, with the core in its $1s^22s^22p$ configuration.) For a given value of the magnetic quantum number, the vector defined by the angular-momentum vector of the p (or d, or $f,\ldots$) electron should play the role played by $\mathbf{R}$ for the Rydberg H_2 problem. For an upnolarized core, one would average over the magnetic quantum number.

IV. CONCLUSIONS

We have shown that the retardation potential obtained using a semiclassical 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 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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APPENDIX A: DISAPPEARANCE OF THE "NONADIABATIC" TERM

The (action-at-a-distance or *instantaneous*) Coulomb potential affecting the distant Rydberg electron is, in the dipole approximation,

$$\frac{-e^2}{r} + \frac{\mathbf{r}_1 \cdot \mathbf{r}}{r^3} \equiv \frac{-e^2}{r} + h. \qquad \text{(A1)}$$

In first order, the effect of the ($\mathbf{R}$ independent) perturbation h averages out to zero. The $1/r^4$ second-order effect of h, $V_{\rm pol}$ of Eq. (2.4), does not involve excitation of the outer electron; E_{vn} never appears. With $\mathbf{r}$ fixed, the outer electron interacts with the dipole moment which its electric field induces in the core; the correlation between the electrons is *static*. E_{vn} does enter in the determination of the $1/r^6$ third-order effect of h, the "nonadiabatic" potential $V_{\rm nonad}$ of Eq. (2.5); we are here concerned with a *dynamic* correlation, with the electrons simultaneously excited, with each electron "aware" at each instant of the location of the other electron at that instant. $V_{\rm nonad}$ can therefore be correct asymptotically only for c infinite. For c finite, $V_{\rm nonad}$ is correct (beyond a few a_0) only out to distances of order r^*, where r^* is defined by the equality of the to-and-fro time of flight of two photons and the period of the inner electron. (See Ref. [2].) Since the argument does not require the unperturbed state of the core electron to be spherically symmetric, it is applicable to Rydberg states not only of He but of H_2.

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