

Polarizability of Rydberg atoms and the dominant long-range interactions

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The dominant long-range interaction of an alkali-metal atom with charged particles at low energies is given for large separation R by the dispersive potential $W \approx -\alpha_d/R^4$ in terms of the dipole polarizability α_d . For atoms prepared initially in Rydberg states of quantum numbers (n, l) , the potential assumes a more complicated form due to the complete or near degeneracy of the n manifold. Contributions to the polarizability are treated in two parts, (a) one for the nondegenerate states and (b) the other for the degenerate or near degenerate cases. It is shown that $\bar{\alpha}_d^{(b)}$ for case (b) is in general R dependent, and in the limit of complete degeneracy, diverges as R^2 . That is, for a small energy gap Δ between a pair of nearly degenerate states which are dipole coupled, the dispersion potential $W^{(b)} \approx D/R^2$ for $R < R_x$ and $W^{(b)} \approx -\alpha_d^{(b)}/R^4$ for $R > R_x$, where D is the dipole moment, $R_x = [2|D/\Delta|]^{1/2}$, and $\alpha_d^{(b)} = D^2/\Delta$. They may also compete with a $1/R^3$ potential for Rydberg atoms with $l > 0$. The total α_d can be very large in magnitude for small Δ and even assume negative values, but the corresponding R_x also increases as Δ decreases. The validity region in R of the R^{-4} behavior of the potential recedes to larger R as the polarizability grows. A general formula for α_d is given, taking into account the effects of fine-structure splitting, the Lamb shift, and quantum defects.

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I. INTRODUCTION

The collision of alkali-metal atoms in their ground states with charged projectiles at low energies is described by the long-range interaction, which is usually given [1–4] in terms of the dipole polarizability α_d . A pair of alkali-metal atoms interacts by a van der Waal's type long-range potential that also depends on the product of electric dipole polarizabilities of participating atoms. However, atoms prepared initially in their excited states interact in a more complex way, mainly due to near degeneracy of the Rydberg states that are dipole coupled to the initial state. The corresponding potential is sensitive to the degree of degeneracy breaking. We present a coherent discussion of the long-range potentials for Rydberg atoms. As will become clear, the polarizability can be very large in magnitude and sometimes can even be negative, but its effect becomes significant only at large distances.

In view of the importance of the long-range interactions involving Rydberg atoms in many applications, such as in cold trapped atoms and plasmas, it is of interest to analyze various theoretical complications in determining the leading polarization potentials. Thus, cold excited atomic gas may be produced, e.g., by laser exciting trapped atoms. Since the polarizability depends on the initial excited states, the long-range potential may be tunable by selectively exciting atoms to specific states. Of course such excited initial states are not stable against radiative and other collisional cascades, and this quasistability must be taken into account in experiments that involve Rydberg atoms. The excited atoms can interact with each other to produce ions and free electrons by molecular autoionization [5]. For a dilute gas of excited atoms, the natural relaxation time can be as long as a fraction of a millisecond for a high-Rydberg state (HRS), while typical collisional relaxation time can be several orders of magnitude shorter, depending on the relative densities of neutral and charged particle mixtures.

The trapped atoms may also be directly ionized by laser irradiation to form a cold plasma. Such a plasma may relax by the recombination of ions and electrons to form Rydberg states via three-body and radiative recombinations. The recombined ions are presumably in excited states, and thus they further relax by collisions of the type discussed here.

Theoretical evaluation of the dipole polarizability α_d for the Rydberg atoms is made complicated by the fact that the n manifold of excited states is nearly degenerate. There are several factors that can break this degeneracy: (i) the l -dependent quantum defects (QD), (ii) fine-structure splitting (FS), and (iii) Lamb shift for the $l=0$ state. (iv) Hyperfine interactions further split levels, but we neglect them here because of the same orbital angular momenta involved for the pair. (v) An external field can remove degeneracy through Stark and Zeeman effects. Points (i)–(iii) are discussed in Sec. III.

We show in this paper that these degeneracy-breaking mechanisms play an important role in determining the long-range behavior of W_d . The degree of degeneracy is a relative concept and in collisions depends on the separation R between the colliding particles. Both the degenerate and near degenerate cases must be treated simultaneously on an equal footing. We derive in Sec. IV a set of dipole polarization formulas that are suitable to nondegenerate, degenerate, and near degenerate cases. A simple configuration-mixing procedure will be adopted to derive a unified form of perturbation theory that is applicable equally to all cases. The resulting polarizability smoothly goes over from one extreme to the other, depending on the degree of degeneracy breaking. The connection between the treatment of polarizability given in Sec. IV and the resonance states found in the electron-hydrogen scattering is clarified in Sec. V. Atomic units are used throughout, with $m = e^2 = \hbar = 1$ and $c = 137$.

II. PRELIMINARY DISCUSSION ON THE POLARIZABILITY

The interaction H' between a charged projectile and target atom may be expanded in multipoles, as $H'(\vec{r}, \vec{R}) = H'_0 + H'_d + H'_q + \dots$, where H'_0 is the monopole interaction, $H'_d = \hat{d}/R^2$ is the dipole interaction, $H'_q = \hat{q}/R^3$ is the quadrupole interaction, etc., at large R . It is assumed in the following that, for the initial target state $|nl\rangle$, R is taken to be $R \gg n^2 a_0$, so that the multipole expansion of H' converges. The operators \hat{d} and \hat{q} , etc., are defined as $\hat{d} = rP_1(\cos \Theta)$ and $\hat{q} = r^2 P_2(\cos \Theta)$, where $\cos \Theta = \vec{r} \cdot \vec{R}/rR$ and \vec{r} is the internal coordinates of the target electrons. A similar expansion is possible for the interaction of an atom with external field $\vec{F}(\vec{R}) = -\vec{\nabla} V_F$, as $H'_{\text{ext}} = H'_{\text{ext}-d} + H'_{\text{ext}-q} + \dots$, where $H'_{\text{ext}-d} = \vec{d} \cdot \vec{F}$, and $H'_{\text{ext}-q} = (1/2)\vec{q} : \vec{\nabla} \vec{\nabla} V_F$, etc. These perturbations affect the target, resulting in the distortion of its electronic orbitals.

Generally, the effective interaction U in the elastic channel P is given by

$$U_P = V_P + W_P, \quad (1)$$

where V_P is the static potential which is usually of short range. (It may contain a q/R^3 potential for $l \neq 0$ from the quadrupole contribution H'_q .) The W_P is the dispersion potential defined in terms of the Green's function G^Q [4], as $W_P = \langle nl | H'_d G^Q H'_d | nl \rangle$. In atomic collisions, this potential is usually long ranged and contains the polarization contribution. We study W_P in the stationary approximation (SA) where the projectile is held fixed at large R .

In the case of nondegenerate target atoms, initially in state $|i\rangle = |g\rangle = |nl\rangle$, the leading contribution to the polarization potential is given to second order in the interaction H'_d

$$W_d(R) \approx -\alpha_d/R^4, \quad (2a)$$

where

$$\alpha_d = \sum_{n'} \sum_{l'} |D(i, n'l')|^2 / \Delta(i, n'l') \quad (2b)$$

with $\Delta(i, n'l') = E_{n'} - E_i \equiv \Delta$ and $D(i, n'l') = \langle i | \hat{d} | n'l' \rangle \equiv D$ with $l' = l \pm 1$. In the following, we omit the state labels involved in Δ and D unless ambiguity arises. The $E_{n'}$'s are the energies of the target atom. As is well known [4], there are additional contributions to the effective potential W coming from the electric quadrupole and dynamical corrections, etc., which are of higher powers in $1/R$. (A small R^{-5} additive correction is present due to the retardation effect.) Formula (2) makes sense when the validity region of R is specified. For $|i\rangle$ equal to the ground state $|g\rangle$, all $E_{n'} > E_g$ and thus $\alpha_d > 0$. But, for $|i\rangle$ equal to the excited states $|nl\rangle$, some of the terms in Eq. (2b) can be negative because of the change in sign of the energy denominators Δ for $n' < n$. The situation is similar to that for the oscillator strengths.

For the initial excited states (nl) , $l > 0$, the quadrupole interaction H'_q is the leading nonzero contribution to the diagonal potential of the type

$$V_q \propto q_{nl}/R^3 \quad (l \neq 0), \quad (3)$$

where $q_{nl} = \langle nl | \hat{q} | nl \rangle \equiv q$. In the pure hydrogenic case, the radial part of q scales as $q_{nl} \propto \langle r^2 \rangle = (n^2/2)[5n^2 + 1 - 3/(l+1)]$; this is to be compared with $\langle r \rangle = [3n^2 - l(l+1)]/2$, while, for example, $D(nl, n'l' = l-1) \propto (3/2)n\sqrt{n^2 - l^2}$ for a degenerate pair. Potential (3) is always present for $l > 0$, independent of the degeneracy question.

We consider in this paper a generalization of formula (2) to the case of nearly degenerate Rydberg atoms, which may be prepared initially in the HRS, $|i\rangle = |nl\rangle$ with large n . The form (2) will break down for systems with degenerate levels. In order to develop a proper treatment of the degenerate case, we first discuss in Sec. III various ways by which degeneracy may be broken in complex atoms.

III. DEGENERACY BREAKING

Rydberg states of complex atoms are shifted from the pure hydrogenic values by internal perturbations. Thus, the effect of the core screening by inner-shell electrons is conveniently described in terms of quantum defects (QD). The spin-orbit coupling [fine structure (FS)] and vacuum polarization effects (the Lamb shifts) also shift levels. The actual form of the polarizability critically depends on these degeneracy-breaking mechanisms. In collisions, the relative degree of degeneracy depends on the relative separation R between the colliding particles. For the present discussion, therefore, we define

$$R_x = \sqrt{2|D/\Delta|}, \quad (4)$$

where D is the dipole coupling matrix element for the two near degenerate levels and Δ is the magnitude of the shift. This parameter R_x separates the regions of R where the relative degrees of degeneracy are different, as explained more fully in Sec. IV.

A. Quantum defects

Consider a complex atom with one or more core electrons and an outer-shell electron in the HRS. Its energies are often represented in terms of l -dependent, but presumably n -independent, quantum defects σ_l , which become small with increasing l . Thus, for the HRS electron, $E_{nl} \approx -1/(n - \sigma_l)^2 \text{Ry}$. The shift due to QD is then $S_{nl}^{\text{QD}} \equiv E_{nl} - E_{nl}^{(0)} = -2\sigma_l/n^3 \text{Ry}$ for large n , where $E_{nl}^{(0)} \equiv -1/n^2 \text{Ry}$. The energy gap Δ_{QD} for the two levels (nl) and $(n'l')$ within the same n manifold of levels ($n = n'$) is then given by

$$\Delta(nl, n'l') \equiv E_{n'l'} - E_{nl} \approx 2(\sigma_l - \sigma_{l'})/n^3 \equiv \Delta_{\text{QD}}. \quad (5)$$

The radial part of the dipole coupling matrix element for the above degenerate pair, with $n' = n$, is given by $D \approx (3/2)n\sqrt{n^2 - l^2}$, for say $l' = l - 1$. For complex atoms in states of low l , the quantum defect can be large, in which

case levels of the same n manifold may not be that close to each other in energies. For example, when $\sigma_l \approx 1$, we may set $n' = n - 1$, $l' = l + 1$, and obtain $\Delta(n'l', nl) \approx (2/n'^3)(\sigma_l - \sigma_{l'} - 1)$. Following Eq. (4), we have $R_x^{\text{QD}} \approx \sqrt{2|D/\Delta_{\text{QD}}|} \approx n^{5/2}/\sqrt{|\sigma_l - \sigma_{l'}|}$. Δ_{QD} is usually the largest for low l , and can often be in the eV range.

B. Fine-structure effect

The fine-structure (FS) shift is given by [6,7]

$$S_{\text{FS}} = \langle nlsj | V_{\text{FS}} | nlsj \rangle, \quad (6a)$$

$$V_{\text{FS}} = -(e\hbar^2/2m^2c^2)(\partial V_{\text{Coul}}/r\partial r)\vec{l} \cdot \vec{s}. \quad (6b)$$

For two states with $l=0$ and $l=1$, we have $S_{\text{FS}}(l=0) = 0$ and $S_{\text{FS}}(l=1) \equiv S_{\text{FS}}$, which give $\Delta_{\text{FS}} = S_{\text{FS}}$ and $R_x^{\text{FS}} = \sqrt{2|D/\Delta_{\text{FS}}|}$. When n is large, $\Delta_{\text{FS}} \propto 1/(c^2n^3)$, so that $R_x^{\text{FS}} \propto n^{5/2}$ for near degenerate cases. In the pure hydrogenic case with $n=2$, for example, we have $\Delta(2p_{3/2} - 2p_{1/2}) = 0.37 \text{ cm}^{-1}$, and thus

$$\alpha_d(2s_{1/2} \rightarrow 2p_{3/2}) > 0 \quad \text{and} \quad \alpha_d(2s_{1/2} \rightarrow np, n > 2) > 0. \quad (7a)$$

On the other hand, for $2p_{3/2}$,

$$\alpha_d(2p_{3/2} \rightarrow 2s_{1/2}) < 0 \quad \text{and} \quad \alpha_d(2p_{3/2} \rightarrow 1s_{1/2}) < 0 \quad (7b)$$

while

$$\alpha_d(2p_{3/2} \rightarrow n's, n'd, n' > 2) > 0, \quad (7c)$$

etc. ($1 \text{ Ry} = 1.1 \times 10^5 \text{ cm}^{-1} = 3 \times 10^9 \text{ Mc/sec}$ and $c = 137$ in a.u.). The magnitude of α for Eq. (7b), for example, is of the order of $\alpha \approx 10^6 a_0^3$ for $n=2$, and rapidly increases for higher n . On the other hand, typically $R_x \approx 10^3 a_0$ and thus, for $R \approx R_x$, $W_d \approx \pm 10^{-6} \text{ Ry}$. This can be compared with a nondegenerate contribution of $W_d^{(a)}(2s) \approx 10^{-10} \text{ Ry}$ at the same value of R .

The Dirac theory gives the hydrogenic states with the same j values degenerate. Thus, the states $2s_{1/2}$ and $2p_{1/2}$ are degenerate, which is eventually broken by the Lamb shift, as discussed below. The levels $3p_{3/2}$ and $3d_{3/2}$ remain degenerate, but for atoms with more than one electron, Δ_{QD} will break this degeneracy. Since the Δ for QD and FS can be either positive or negative, depending on particular situations, the resulting α from such a pair can assume either sign.

C. Lamb shift

The effective interaction that produces the Lamb shift is given [8] by

$$S_L = \langle nl | V_L | nl \rangle, \quad (8a)$$

$$V_L = (4/3c^3)[\ln(mc^2/2E_{\text{ave}}) + 19/30]\delta(\vec{r}) \text{ Ry}. \quad (8b)$$

Operator (8b) affects only the $l=0$ orbitals and we have generally $S_L \propto m/(Mc^2n^3)$, where m and M are the electron and nuclear masses, respectively. In hydrogen, it shifts the

$2s_{1/2}$ level up from the originally degenerate $2p_{1/2}$ by 0.035 cm^{-1} , while the $3s_{1/2}$ by 0.010 cm^{-1} up from $3p_{1/2}$. Thus, for hydrogenic $2s_{1/2}$ and $2p_{1/2}$, we have $S_L(2p_{1/2}) = 0$ and $\Delta_L = S(2s_{1/2})$. $R_x^L = \sqrt{2|D/\Delta_L|}$. On the other hand, the gap Δ between the $2s_{1/2}$ and $2p_{3/2}$ states is 0.33 and 0.098 cm^{-1} between $3p_{3/2}$ and $3s_{1/2}$. (Note that $3p_{3/2}$ and $3d_{3/2}$ are still degenerate.) This gives $\alpha_d(2s_{1/2} \rightarrow 2p_{1/2}) \approx D^2/\Delta_L \approx 10^7 a_0^3$. In the region $R > R_x^L \approx 10^4 a_0$, for example, where α_d is presumably valid (Sec. IV), we expect the polarization potential $W_d \approx -\alpha_d/R^4 \approx 10^{-8} \text{ Ry}$, which may be compared with a typical nondegenerate contribution $W^{(a)} \approx 10^{-15} \text{ Ry}$ at the same R . (At $R = 10^2 a_0$, $W^{(a)} \approx 10^{-7} \text{ Ry}$.) Continuing this example of the hydrogenic case, with $n=2$ and the Lamb shift taken into account, we have

$$\alpha_d(2s_{1/2} \rightarrow 2p_{1/2}) < 0,$$

$$\alpha_d(2p_{1/2} \rightarrow 2s_{1/2}) > 0,$$

and

$$\alpha_d(2p_{3/2} \rightarrow 2s_{1/2}) < 0.$$

Similar inequalities may be obtained for $n > 2$ for both hydrogenic and nonhydrogenic cases.

Dipole polarizability associated with a pair of nearly degenerate levels can be very large and assume either sign. All three shifts S 's and gaps Δ 's discussed above behave at large n as $1/n^3$, resulting in $R_x \propto n^{5/2}$. Combining these cases, we define the total shift

$$\Delta = \Delta_{\text{QD}} + \Delta_{\text{FS}} + \Delta_L, \quad (9)$$

where one or more of the HRS may be zero or negative, depending on the choice of the state $|nl\rangle$. Some cancellations among the terms in Eq. (9) are possible. Generally, the magnitude of Δ_{QD} is the largest among the three for $l < 3$, but becomes comparable to Δ_{FS} at larger l . Δ_L for $l=0$ is usually an order of magnitude smaller than Δ_{FS} . For the excited HRS with large l , Δ_{QD} becomes very small while Δ_{FS} becomes relatively more important.

IV. STATIONARY DIPOLE POLARIZABILITY OF EXCITED ATOMS

To extend the polarization potential (2) for the nondegenerate case to excited atoms in state (nl) , which is nearly degenerate with other dipole-coupled states, it is convenient to treat the problem in two parts: (a) one that involves only the nondegenerate states (n', l') , with $n' \neq n$, and (b) the second part that involves states which are near degenerate and that usually involves states of the same manifold, $n' = n$. This division is arbitrary, but facilitates the analysis without affecting the final result. Part (a) can be treated by the conventional method via Eq. (2), while part (b) requires a special reformulation. While the conventional procedures treat the degenerate and nondegenerate cases separately [6], we will present a unified approach in Sec. IV B.

We set

$$\alpha_d = \alpha_d^{(a)} + \alpha_d^{(b)}. \quad (10)$$

A. Nongenerate case (a)

As in Eq. (2), we define the dipole polarizability

$$\alpha_d^{(a)} = \sum_{n' \neq n} \sum_{l' = l \pm 1} |\langle nl | \hat{d} | n' l' \rangle|^2 / (E_{n' l'} - E_{nl}), \quad l' = l \pm 1. \quad (11)$$

$\alpha_d^{(a)}(nl)$ is of order unity when n for the initial state is small, but for high Rydberg states with large n the dipole matrix elements D become very large ($\propto n^2$). In addition, the energy denominators become very small for n' close to n . Therefore, the dominant contributions to $\alpha_d^{(a)}$ may be estimated rather simply by taking into account only a few nearest-neighbor states, because of the $1/\Delta$ weighting in Eq. (11). Obviously, there will be sizable cancellations among the contributions from those states which lie above and below the state (nl) . Generally, α_d becomes large in magnitude with increasing n because of its n dependence $\alpha_d \propto n^7 a_0^3$. On the other hand, for $R > n^2 a_0$, $W_d \approx -\alpha_d / R^4 \propto 1/n$.

The sum over n' in Eq. (11) may be replaced by the integrals, as

$$\alpha_d^{(a)} = \sum_{l'} \langle nl | \hat{d} | X_{l'} \rangle, \quad (12)$$

where $l' = l \pm 1$, and X satisfies the equation

$$[h(\vec{r}) - E_{nl}] X_{l'} = \hat{d} | nl \rangle - a_{l'} | nl' \rangle, \quad (13)$$

and where $a_{l'}$ is a Lagrangian multiplier, introduced here to make X orthogonal to $|nl'\rangle$. Note that the term with $n' = n$ is excluded in the sum in Eq. (11).

B. Degenerate case (b)

A perturbation theory is needed that covers both the degenerate and near degenerate cases simultaneously. This is achieved by simply taking the relevant sets of states (usually pairwise at a time) which lie close in energy and mixing them. The task of estimating the polarizability is simplified by the fact that the coupling potential is of the form $H'_d \approx \hat{d}/R^2$. We are here interested in the leading term in the effective potential at large R , so that the level mixing by H'_d needs to be taken only to second order, i.e., the mixing of two nearest-neighbor levels at a time. We denote the two states selected for mixing by 1 and 2 with energies E_1 and E_2 which contain all the effects of shifts S . Then, the energy matrix to be diagonalized is

$$\begin{vmatrix} E_1 - E & M'_{12} \\ M'_{12} & E_2 - E \end{vmatrix} = 0, \quad (14)$$

where $M'_{12}(R) = \langle 1 | H'_d | 2 \rangle = D(12)/R^2$ with $D(12) = \langle 1 | \hat{d} | 2 \rangle \equiv D$. We obtain

$$E = \bar{E} \pm 0.5 \sqrt{\Delta_{12}^2 + 4M'_{12}(R)^2}, \quad (15)$$

where $\bar{E} = (E_1 + E_2)/2$. $\Delta(12) = E_2 - E_1 \equiv \Delta$ can assume either a positive or negative sign.

Now consider several special cases.

1. $\Delta \approx 0$, i.e., $\Delta^2 < 4M'_{12}{}^2$; case (b)

We have

$$E \approx \bar{E} \pm M'_{12} = \bar{E} \pm D/R^2 \equiv \bar{E} \pm \tilde{\alpha}^{(b)}(R)/R^4, \quad (16)$$

where $\tilde{\alpha}^{(b)}(R) = DR^2$ if we follow the convention (2). Obviously, this polarizability goes to infinity as R increases and the potential becomes

$$W_d^{(b)} \approx D/R^2. \quad (17)$$

The expression (16) is limited to the region of $R < R_x$ where, following Eq. (4) and for the parameters defined above,

$$R_x = [2|D/\Delta|]^{1/2}. \quad (18)$$

Therefore, the limit $\Delta \rightarrow 0$ is accompanied by $R_x \rightarrow \infty$; that is, the region of R where Eq. (17) is valid expands as Δ decreases.

2. $\Delta^2 > 4M'_{12}{}^2$; case (a)

This is similar to the nondegenerate case (a), and we expect the result to be the same as that obtained in Sec. IV A. For $R > R_x$, $|\Delta|$ becomes relatively larger than $|M'_{12}|$, and we have instead of Eq. (16)

$$E \approx \bar{E} \pm \Delta \pm W_d, \quad W_d = -\alpha_d^{(a)}/R^4, \quad (19)$$

which is the result expected from the nondegenerate perturbation theory. With the usual R^{-4} behavior factored out, we have

$$\alpha_d^{(a)} \approx D^2/\Delta. \quad (20)$$

Here Δ can be positive or negative. For $|\Delta|$ small, the magnitude of the polarizability becomes large, but R_x also increases. This behavior is one of the main results of this study; as $\Delta \rightarrow 0$, $\alpha_d^{(a)} \rightarrow \infty$, but at the same time $R_x \rightarrow \infty$ as well. That is, as Δ decreases the region of R where Eqs. (20) and (19) are valid recedes to infinity while the region of R for the cases represented by Eqs. (16) and (17) expands.

Incidentally, any other potentials of the type $1/R^2$, such as the centrifugal potential, can be included in the above diagonalization procedure with minimal changes. (See Sec. V.)

3. Intermediate region of $R \approx R_x$

We have a smooth transition between the two extreme cases (a) and (b); Eq. (15) may be written in the form

$$\mathcal{E}(R) = \bar{E} \pm (D/R_x^2) [1 + (R_x/R)^4]^{1/2}, \quad (21a)$$

where R_x and R are directly compared, and thus

$$W(R) \equiv \mathcal{E}(R) - \mathcal{E}(R \rightarrow \infty) \equiv -\tilde{\alpha}_d(R)/R^4. \quad (21b)$$

Polarization of Rydberg atoms by an external electric-field perturbation is similar to the collisional case in the stationary approximation. As an external field \vec{F} distorts the target, we have a new parameter $F_x^{-2} \approx 2D/\Delta$, which replaces R_x^2 . All the relations defined for the collisional case are recovered by the substitution $F \rightarrow 1/R^2$.

4. Multiple nearly degenerate levels

The procedure described above in Secs. IV B 1–IV B 3 may be easily generalized to cases in which more than two levels are nearly degenerate, such as for targets in HRS where large n and l are examples, and where Δ_{QD} are negligibly small. [The other terms in the total Δ of Eq. (9) can be significant.] Since we are interested in the leading order of $1/R$ for large R , only the diagonal and the two terms next to the diagonal terms that represent dipole coupling are relevant. This feature greatly simplifies the problem in that the mixing takes place only pairwise. Therefore, the results of Secs. IV B 1–IV B 3 are essentially unchanged; the final potential is given simply by a sum of the contributions from the individual pairs, with $l' = l \pm 1$.

C. Evaluation of α_d

The auxiliary function X introduced in Eq. (12) for $\alpha_d^{(a)}$ may be evaluated easily by a series solution. For example, for $(nl) = 2s$ of hydrogen, we set

$$X_{l'=1}(r) = (r^2/2) \sum_{m=0} b_m r^m \exp(-r/2) \quad (22)$$

with the result b_0 is arbitrary, $b_1 = 0$, $b_2 = \frac{1}{10}$, $b_3 = \frac{1}{60}$, $b_4 = \frac{1}{560}$, etc. The constant b_0 is adjusted to make the function X orthogonal to the $2p$ orbital, while $b_m = (m-1)/[(m+2)(m+1)-2]b_{m-1}$, for $m > 3$. This is similar to the polarized orbital procedure [2].

Alternatively, a semiclassical Green's function G_{sc}^0 may be used [9] in the evaluation of $\alpha^{(a)}$ and W_p . Thus, for states with angular momentum l , we have the radial Green's function

$$g_l(r, r') = (4/\pi m) \int_{P_{l1}}^{P_{l2}} p^2 dp j_l(pr) j_l(pr') / P_l^2, \quad (23)$$

where $P_l(u) = -\{2m[E_i - L^2/u^2 - V(u)]\}^{1/2}$ with $u = r - r'$ and $v = (r + r')/2$. The limits of integration P_{l1} and P_{l2} are similarly defined, with u replaced by v . $L = l + \frac{1}{2}$. For a full Green's function covering the entire spectrum, we have $P_{l1} = 0$ and $P_{l2} = \infty$.

The polarization potential may also be viewed as a fluctuation potential [10] affecting the collision via virtual excitation of the target. In the closure approximation, the sum in Eq. (2) for α collapses when an average excitation energy \bar{E} is introduced, as

$$\alpha_d^{fl} = [\langle nl | \hat{d}^2 - \langle \hat{d} \rangle^2 | nl \rangle] / (\bar{E} - E_{nl}), \quad (24)$$

where $\langle \hat{d} \rangle \equiv \langle nl | \hat{d} | n'l' \rangle \equiv d$ for $l' = l \pm 1$. The form (24) is useful in determining the magnitude of cancellations involved in the excited-state polarizability and also its overall sign.

Summarizing the result obtained above, the dominant long-range potential for an excited atom in state $(n, l=0)$ and interacting with charged projectile is of the form $W \propto D/R^2$ for $R < R_x$ and $W \propto -\alpha_d^{(b)}/R^4$ for $R > R_x$. On the other hand, the $l > 0$ case requires three regions of R defined by $R_{qD} = |q/D|$ and $R_{dq} = |\alpha_d/q|$, with $R_{qD} \propto n^2$ and $R_{dq} \propto n^3$. Generally $R_{qD} < R_x < R_{dq}$, where $R_x \propto n^{5/2}$. For $R < R_{qD}$, the dipole potential D/R^2 dominates, and in the region $R_{qD} < R < R_{dq}$, the direct quadrupole potential q/R^3 is important. Finally, for $R > R_{dq}$, the potential changes to $W \propto -\alpha_d/R^4$.

V. RESONANCES AND DYNAMICAL EFFECTS ON THE POTENTIAL

In the scattering of charged particles off hydrogen, sets of resonances are produced [11] for scattering energies just below each of the n th excitation thresholds, adjusted by a cut-off due to Lamb shifts that break the degeneracy. This is attributed to the $ns-np$ degeneracy, which produces a diagonal potential of $1/R^2$ type, which can in principle support an infinite number of ‘‘bound’’ states. The polarizability in case (a) is given by the sum of contributions from these resonance states.

A. Two-channel problem

In the two-channel problem of electron hydrogen scattering near the $n=2$ threshold, where the $2s$ and $2p$ channels are nearly degenerate ($\Delta_{\text{QD}}=0$ and $\Delta_{\text{FS}}=0$ for $j=\frac{1}{2}$), two coupled equations for the scattering particle may be set up, as

$$[K + V_i - e_i]u_i = -V_{ij}u_j, \quad (25)$$

where $i, j = 1$ and 2 , and $V_{ij} = \langle i | H'_d | j \rangle$. The total energy E is given by $E = E_i + e_i$ for the atom (E_i) and projectile (e_i), with $e_1 = e_2 \equiv e_c$. V_i may be neglected because they are short-ranged, and for dipole coupling, V_{ij} behaves as D/R^2 . We can treat this by simply defining $u_{\pm} = (u_1 \pm u_2)/2$, which gives immediately [11]

$$[K - e_c + V_{12}]u_{+} = 0. \quad (26)$$

(One of the V_i contains the centrifugal potential V_l , but the above procedure can readily be modified; of course the mixing will not be of a 1 to 1 ratio, but the above result will not change in its essential contents. This was also noted in Sec. III). Now, the diagonal potential is of long-range $1/R^2$ type. The resonances observed in the e -H collisions near the $n=2$ threshold are thus attributed to this potential. However, the number of resonances is made finite by the cutoff at the energies associated with the Lamb shift, where the assumed degeneracy between the $2s$ and $2p$ ($j=\frac{1}{2}$) is broken. Hence this is consistent with the picture derived for case (b) in Secs. III C and IV B.

In this respect, the resonances observed in the e -H scattering system are not quite the Breit-Wigner-type quasibound compound resonances, a Q type (commonly called the Feshbach resonances) where strong correlations among the actively interacting particles are present. Rather, they are somewhat close to the potential shape resonances, a P type, because they come from the Rydberg-level state degeneracies and are associated with the $1/R^2$ potential. Therefore, we may designate them as “dipole resonances” [11]. Furthermore, this is in contrast with those resonances that appear throughout the neutral and charged ions, as multiply excited states, at energies close to the individual excitation energies associated with pure Coulomb values. We may identify them as “Rydberg resonances;” they are also close to the potential resonances. Evidently, in atoms and ions, the central Coulomb field of the nucleus plays a dominant role, while the inner-core electrons predominantly play the role of screening this field. Thus, the outer Rydberg electrons are largely controlled by the screened central Coulomb field.

B. Stationary vs adiabatic approximations

In view of the sensitivity of the polarizability on the energy denominators in the expression (2), we reexamine its origin for the purpose of obtaining possible dynamical corrections to W . For the collision of charged particles with excited atomic targets, the effective potential in the elastic channel is given by [4]

$$W_{nl} = \langle nl | H' G^Q H' | nl \rangle, \quad (27)$$

where

$$G^Q = [Q(E - K - h - H')Q]^{-1}. \quad (28)$$

Here, h is the target Hamiltonian and K is the kinetic energy operator for the projectile. The projection operator Q is defined by $Q \equiv Q_{nl} = 1 - P_{nl}$, where $P_{nl} = |nl\rangle\langle nl|$. That is, Q spans the space orthogonal to $|nl\rangle$; for example, $Q \approx \sum_{n', \Sigma_{l'}} |n'l'\rangle\langle n'l'|$ with $l' = l \pm 1$.

The polarizability in the stationary approximation (sa) is defined by setting $(K + H' - e_{nl}) = 0$ in G^Q , where $E = E_{nl} + e_{nl}$ and E_{nl} are the eigenvalues of the target Hamiltonian h . Then, we have $G_{sa}^Q = [Q(E_{nl} - h)Q]^{-1}$ and $W_{sa}(R) = \langle nl | H' G_{sa}^Q H' | nl \rangle$. The singular nature of the polarizability comes from the vanishing of the new denominator $Q(E_{nl} - h)Q$, i.e., at $E_{nl} \approx E_{n'l'}$. Obviously, the situation changes if the neglected term in $G_{sa}^Q \langle n'l' | (K + H' - e_{nl}) | n'l' \rangle$, is not small.

On the other hand, in the usual adiabatic picture, one calculates the potential energy for each fixed R . Aside from a slight adjustment in the choice of Jacobi coordinates used, such a potential may be defined in terms of the adiabatic Green's function [12] defined by

$$G_{ad}^Q = [Q(e_{nl} + W_{ad}(R) - h - H')Q]^{-1}, \quad (29a)$$

$$W_{ad}(R) = \langle nl | H' G_{ad}^Q H' | nl \rangle. \quad (29b)$$

Note that Eq. (29) is nonlinear in W_{ad} because W_{ad} appears also in G_{ad}^Q . To second order in H' , G_{sa}^Q gives the same result as that with G_{ad}^Q , except when G^Q is singular.

C. Degenerate case (b)

Now we compare the two G^Q 's for the degenerate case (b) with $n' = n$, where the denominator of G_{sa}^Q vanishes. It was shown [4] in the nondegenerate case that the effect of K in G^Q is to yield a dynamical correction to the adiabatic potential, which is of higher power in $1/R$ than $W_d^{(a)}$. Thus, for nondegenerate cases, both G_{sa}^Q and G_{ad}^Q yield the same potentials in so far as the leading term in $1/R$ is concerned. But, for degenerate cases W_{ad} in G_{ad}^Q of Eq. (29a) can be of a dipole form which can seriously alter the spectrum. The comparison between G_{sa}^Q and G_{ad}^Q is more complicated in the degenerate case and requires more careful analyses.

We have to this point omitted one important aspect of the collisions involving excited targets. In addition to the dispersive part, G^Q for the Rydberg atom should also contain an absorptive part which has not been dealt with; for high n , there are many open channels and overlapping branch cuts in energy space, which broaden the resonance levels. It is not clear whether the two or more near degenerate and broadened channels can produce a potential that still behaves as $1/R^2$ and/or $1/R^4$. This problem, together with the radiative channel coupling and possible cooperative processes in cold excited gases, such as the molecular autoionization, will be discussed elsewhere.

VI. DISCUSSION AND SUMMARY

We have examined the long-range behavior of the Rydberg-atom charged-particle interaction and shown that for near degenerate levels, the dispersive dipole potential W_d is dominated by the $1/R^2$ -type behavior for $R < R_x$, and it gradually switches over to the $1/R^4$ type interaction at $R > R_x$, often with very large polarizability. We obtained the general result by treating both degenerate and nondegenerate cases simultaneously; the conventional configuration-mixing procedure provides a unified treatment. When the energy gap Δ between two adjacent levels coupled by the dipole operator H'_d is small, the polarizability is dominated by the (b) term, $\alpha_d^{(b)}$ of Eq. (21). Experimental study of this behavior may be warranted, as it affects the behavior of a cold excited gas and cold plasmas at low density, where average interatomic separation is large.

We summarize the result discussed in this paper on the dominant long-range potential for Rydberg atoms. Firstly, with $l=0$, we have $U \approx D/R^2$ given by Eq. (17) for $R < R_x$, followed by the $U \approx -\alpha_d^{(b)}/R^4$ type potential (19) for $R > R_x$ with a large polarizability (of either sign), and where $R_x = \sqrt{2|D|\Delta}$. For $l > 0$, we start with the $U \approx D/R^2$ type for $R < R_{qD}$, where $R_{qD} = |q/D|$, followed by $U \approx q/R^3$ in the region $R_{qD} < R < R_{dq}$, where $R_{dq} = |\alpha_d/q|$. Finally we have the $U \approx -\alpha_d/R^4$ potential for $R > R_{dq}$. It is somewhat strange that the dominant long-range behavior of $W \propto R^{-\gamma}$ is such that, as R gets large, γ also increases. For atoms with

polarizable cores and two or more valence electrons, and for excited atom-atom collisions, situations analogous to the above appear that are associated with the cross polarization [13] when states of the core electrons are degenerate. [See the form in Eq. (31b) below.] Two HRS electrons, whether they belong to the same atom or to two different atoms, must also be treated in the same way as in Sec. IV when the full degeneracy problem is to be taken into account. The dominant long-range behavior of U thus depends on the parameters n , l , D , q , Δ , and α_d , and also on the regions of R of interest, as specified by R_{qD} , R_x , and R_{dq} .

Rydberg-atom–Rydberg-atom collisions in cold excited atomic gas are mediated at large R by a van der Waal's (vdW)–type potential [14] that depends on the product of two α 's, hence it is sensitive to the polarizability. The basic interaction between two alkali-metal atoms A and B ($=A$), for example, is given by [5,14]

$$H' \simeq -(\vec{d}_A \cdot \vec{d}_B + d_{Az} d_{Bz})/R^3. \quad (30)$$

The dispersion potential W is then given in second order in H' , and by the Green's function G_{sa}^Q which factorizes to a form $G_A^Q G_B^Q$ when the convolution integral over the energy is approximated. Thus, for excited atoms in the $l=0$ state, we have

$$W_P \simeq D_A D_B / R^3 \quad \text{for } R < R_x, \quad (31a)$$

$$W_P \simeq -\alpha_A \alpha_B / R^6 \quad \text{for } R > R_x, \quad (31b)$$

and at even larger R we expect $W \propto 1/R^7$ due to the retardation effect. [The cross-polarization term assumes the form

similar to Eq. (31b), with the R^{-6} replaced by $(r_1 r_2)^{-3}$. Therefore, a modification of the type (31a) is relevant for the degenerate case.] The crossover point between Eqs. (31a) and (31b) is R_x , given by

$$R_x \simeq |D_A D_B / (\Delta_A \Delta_B)|^{1/3}, \quad (32)$$

which is to be compared with a quadratic power dependence in Eq. (18). For near degenerate cases, both the α 's and R_x can be very large. Thus, the possibility of a repulsive vdW potential at large separation exists when atoms A and B are selectively excited such that α_A and α_B assume signs different from each other. For $l \neq 0$, V_P assumes a form $V_P \simeq d_A d_B / R^3$, analogous to Eq. (31), for all R ($> n^2 a_0$). This is also the case with weak external electric-field perturbation [15]. Detailed treatment of the interaction between Rydberg atoms will be given elsewhere.

The collisional lifetime of an excited cold gas may be estimated using the vdW interaction [5], modified by Eq. (31), for example. Since the system is radiatively unstable, the time required to accelerate a pair to each other from a large R initially is critical, as the collisional relaxation occurs only at relatively shorter distances. The possibility of observing the effect of degeneracy and retardation on the polarization potential discussed in this paper is being examined for the presently attainable density and temperature, $N_A \simeq 10^9 \text{ cm}^{-3}$ and $T_A \leq 1 \text{ mK}$.

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