

Interaction between a Rydberg atom and neutral perturbers

Ning Yi Du and Chris H. Greene

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

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A simple combination of quantum defect theory with a nonperturbative Fermi-type analysis is shown to reliably determine a class of molecular Born-Oppenheimer potential curves. Applications to alkali-metal-atom-rare-gas-atom dimers verify that their potential curves are determined to semiquantitative accuracy using two pieces of information: the alkali-atom quantum defects and the electron-rare-gas scattering phase shifts.

In quantum mechanics one is often faced with a system composed of two or more simpler subsystems, each of which is separately understood. A fundamental question of some practical importance arises naturally: To what extent can the properties of the composite system be predicted using only the scattering properties of the simpler subsystems, i.e., without solving the full Schrödinger equation for all particles? In an early effort of this type, Fermi obtained a simple formula¹ for the energy levels of a Rydberg atom $A(nlm)$ in the presence of a neutral perturber B located on the quantization axis at $\mathbf{R} = R\hat{z}$, namely,

$$E_{nlm}(R) = E_n^{(A)} - 2\pi L |\psi_{nlm}(\mathbf{R})|^2. \quad (1)$$

Here $L = \lim_{k \rightarrow 0} (\tan \delta_0/k)$ is the s -wave e - B scattering length, and $E_n^{(A)}$ and $\psi_{nlm}(\mathbf{R})$ are the unperturbed energy and wave function for the Rydberg electron moving in the field of the ion core A^+ .

The simplicity of Fermi's treatment contrasts sharply with the best methods used currently.^{2,3} Pascale's formulation² starts, for instance, by finding elaborate l -dependent pseudopotentials which can reproduce the e - A^+ quantum defects and the low-energy e - B scattering phase shifts as accurately as possible. After the pseudopotentials are determined, the full one-electron Hamiltonian is diagonalized at each R in some large variational basis set. While this approach is less transparent than Fermi's, it has accounted quantitatively for many experimental features observed in alkali-metal-rare-gas systems which cannot be explained by Eq. (1), including the alkali absorption spectrum in the presence of a perturbing buffer gas.⁴

The aim of this Rapid Communication is to show how a treatment approaching the simplicity of Fermi's describes molecular potential curves (or their equivalent adiabatic quantum defects) surprisingly well. It adopts much of the philosophy given in the preceding paragraph; the main differences are the following. (i) The pseudopotential representing the e - B interaction is simplified to such an extreme (Dirac δ function) that its Schrödinger equation is exactly solvable. (ii) By using quantum defect theory to represent the Rydberg electron wave function in the field of the ion A^+ , the need for the e - A^+ pseudopotential is eliminated altogether. (iii) The final results are expressed in terms of a smooth R -dependent reaction matrix which directly describes scattering processes $l \rightarrow l'$ caused by

the perturber.

The only *approximate* feature in this outline is the use (i) of an unrealistically oversimplified e - B pseudopotential. If highly accurate wave functions and molecular potential curves are needed for any particular application, it is straightforward to replace the approximation (i) by a variational R -matrix treatment⁵ of a physically reasonable e - B interaction, such as that of Ref. 2. Nevertheless, we show below that the crude approximation (i), which is far simpler and faster to implement numerically, successfully describes most features of the potential curves.

In the following, we consider the simplest such problem: an alkali atom A interacting with a single rare-gas perturber B . Prior to imposing boundary conditions at large electron distances $r \rightarrow \infty$, a set of independent multichannel wave functions is characterized by a real, symmetric body-frame reaction matrix $K_{ll'}(R)$,

$$\psi_{l'}(\mathbf{r}, R) = \sum_l Y_{l\lambda}(\hat{\mathbf{r}}) [f_l(r) \delta_{ll'} - g_l(r) K_{ll'}(R)]. \quad (2)$$

In Eq. (2), (f_l, g_l) are the usual energy-normalized Coulomb wave functions⁶ evaluated at the appropriate electronic energy $\varepsilon(R)$, while \mathbf{r} is the electron position relative to the positive ion A^+ . The perturber B is located on the body-frame quantization axis at $\mathbf{R} = R\hat{z}$ relative to A^+ , whereby λ is conserved. This expression is essentially exact for $r > R + \max(r_A, r_B)$, with r_B the radius of the perturber and r_A the radius of A^+ . The reaction matrix depends on λ and weakly on $\varepsilon(R)$. Once it is known, the discrete electronic energies $\varepsilon(R)$ are the roots of a determinantal equation

$$\det[\tan(\pi\nu) \delta_{ll'} + K_{ll'}(R)] = 0,$$

where $\nu \equiv [-2\varepsilon(R)]^{-1/2}$, which ensures that the bound-state wave function decays exponentially at large r . Denoting the eigenvalues of $K_{ll'}(R)$ by $\tan[\pi\mu_a(R)]$, the allowed energies are thus quantized in terms of a positive integer n by a Rydberg formula for each eigenchannel (in a.u.):

$$\varepsilon_{na}(R) = -\frac{1}{2[n - \mu_a(R)]^2}. \quad (3)$$

At this point, we introduce the ansatz that the e - B interaction potential can be approximated by

$$V_{e-B}(\mathbf{r}) = V_0 \delta(\mathbf{r} - \mathbf{R}). \quad (4)$$

This potential represents only that part of the interaction which affects the s -wave component ($l_0=0$) of e - B scattering. (A small p -wave correction can be non-negligible at $R \lesssim 10$ a.u. and will be added perturbatively below.) Our derivation of the reaction matrix consists of two parts. First, the electronic Schrödinger equation will be solved in integral form for an electron moving in the joint potentials of A^+ and of B [Eq. (4)]. This can be solved in closed form after using a truncated partial-wave expansion $\psi_{l'} = \sum_l Y_{l\lambda}(\hat{\mathbf{r}}) M_{ll'}(r)$, for the l' -th independent solution. The coupled integral equations satisfied by $M_{ll'}(r)$ have the form

$$M_{ll'}(r) = F_l(r) \delta_{ll'} + \sum_{l''} \int dr' \mathcal{G}_l(r, r') V_{ll''}(r') M_{l'l''}(r'), \quad (5)$$

with

$$V_{ll''}(r') = (V_0/R^2) Y_{l\lambda}^*(\hat{\mathbf{R}}) Y_{l''\lambda}(\hat{\mathbf{R}}) \delta(r' - R). \quad (6)$$

The atomic (A) radial Green's function

$$\mathcal{G}_l(r, r') = \pi F_l(r <) G_l(r >)$$

is given in terms of quantum-defect-shifted Coulomb functions for $r > r_A$ which are, respectively, regular and irregular when continued back to the ionic origin,

$$\begin{aligned} F_l(r) &= f_l(r) \cos(\pi\eta_l) - g_l(r) \sin(\pi\eta_l), \\ G_l(r) &= f_l(r) \sin(\pi\eta_l) + g_l(r) \cos(\pi\eta_l). \end{aligned} \quad (7)$$

$$\begin{aligned} K'_{n_a, l} &= K'_{l, n_a} \equiv \left[\sum_{l' (\geq n_a)} |a_{l'}|^2 \right]^{-1/2} \sum_{l'' (\geq n_a)} a_{l''} \bar{K}'_{l'' l}, \quad (l < n_a), \\ K'_{n_a, n_a} &\equiv -\text{sgn}(D) \sum_{l (\geq n_a)} |a_l|^2. \end{aligned} \quad (11)$$

The remaining quantities in Eq. (11) are

$$\begin{aligned} a_l &= |D|^{1/2} F_l(R) Y_{l\lambda}(\hat{\mathbf{R}}), \\ D &= (\pi V_0/R^2) \left[1 - (\pi V_0/R^2) \sum_{l''} |Y_{l''\lambda}(\hat{\mathbf{R}})|^2 F_{l''}(R) G_{l''}(R) \right]^{-1}. \end{aligned} \quad (12)$$

The ε - and R -dependent constant V_0 is now determined by a consistency requirement. The net phase change induced in the wave function close to the perturber must equal the experimental s -wave phase shift $\delta_{l_0=0}$ experienced by a *free* electron which encounters $V_{eB}(\mathbf{r})$. The energy of this free electron is the kinetic energy at \mathbf{R} ,

$$T_e \equiv \frac{1}{2} k^2 = \varepsilon(R) + 1/R. \quad (13)$$

The desired relation is found by solving Eq. (5) again, only using free-particle solutions,

$$\begin{aligned} f\tilde{l} &= (2k/\pi)^{1/2} r j_l(kr), \\ g\tilde{l} &= (2k/\pi)^{1/2} r n_l(kr), \end{aligned}$$

in place of the atomic (F_l, G_l), and, of course, using the

The experimental atomic quantum defects η_l are then taken from standard references.

The coupled equations (5) can be solved trivially, giving a simple reaction matrix \bar{K} relative to the atomic radial solutions (F_l, G_l):

$$\bar{K}'_{ll'}(R) = - \frac{C F_l(R) Y_{l\lambda}^*(\hat{\mathbf{R}}) F_{l'}(R) Y_{l'\lambda}(\hat{\mathbf{R}})}{1 - C \sum_{l''} |Y_{l''\lambda}(\hat{\mathbf{R}})|^2 F_{l''}(R) G_{l''}(R)}, \quad (8)$$

where $C = \pi V_0/R^2$. This result is one of the key formulas of the present study. The numerator of Eq. (8) is just the first-order Born approximation to $\bar{K}'_{ll'}$. Inclusion of higher-order scattering processes is thus seen to rescale every matrix element by the same constant (which depends on ε and R). The resulting matrix (8) is readily transformed into the more usual (f_l, g_l) representation of Eq. (2) through the relation

$$\underline{K} = [\bar{K} + \tan(\pi\eta)] [I - \tan(\pi\eta) \bar{K}]^{-1}, \quad (9)$$

in which η is a diagonal matrix containing the atomic quantum defects. The dimension of \underline{K} is $(l_{\max} + 1) \times (l_{\max} + 1)$ ($\nu < l_{\max} \leq \nu + 1$). For any $l_{\max} \geq n_a$ (n_a being the number of nonzero atomic quantum defects), there are only $n_a + 1$ nonzero eigenvalues $\tan(\pi\mu_a)$ of \underline{K} ,⁷ which can therefore be found by diagonalizing an effective reaction matrix $\underline{K}^{\text{eff}}$ of dimension $(n_a + 1) \times (n_a + 1)$:

$$\underline{K}^{\text{eff}} = [I - \tan(\pi\eta) \underline{K}']^{-1} [\underline{K}' + \tan(\pi\eta)]. \quad (10)$$

Here an auxiliary matrix \underline{K}' has been introduced such that $K'_{ll'} \equiv \bar{K}'_{ll'}$ for $l, l' < n_a$, and where

free-particle Green's function

$$\mathcal{G}_l(r, r') = \pi f\tilde{l}(r <) g\tilde{l}(r >).$$

This procedure yields a free-electron reaction matrix having the structure (8). Its lone nonzero eigenvalue must coincide with the experimental $\tan\delta_{l_0=0}$ for e - B scattering,

$$\tan\delta_0 = \frac{-C \sum_l |f\tilde{l}(R) Y_{l\lambda}(\hat{\mathbf{R}})|^2}{1 - C \sum_l |Y_{l\lambda}(\hat{\mathbf{R}})|^2 f\tilde{l}(R) g\tilde{l}(R)}. \quad (14)$$

Equation (14) thus determines $V_0 = CR^2/\pi$ analytically in terms of the known e - B phase shift for each choice of R and of $\varepsilon(R)$, without any matrix manipulations.

Several details of the above procedure deserve elaboration. First of all, it is essential that the partial wave expansions be truncated to the same l_{\max} in the free-particle expression (14) as in the atomic expression (8). In fact, the summations in the denominators of Eqs. (8) and (14) are formally divergent if the summations are carried out to $l \rightarrow \infty$. This reflects the fact that a Dirac δ function is too highly singular to give an analytically solvable Schrödinger equation in *three* dimensions. Despite this singularity, stable and converged results are obtained when the same l_{\max} is used in both calculations. Our treatment is in some sense a "renormalization" which can produce accurate reaction matrices even though it deals with a highly singular δ -function potential. A second point concerns the dominance of the $l_0=0$ partial wave in the e - B scattering amplitude. At low k values, the s -wave phase shift is expected to predominate, but the Coulombic contribution to the electron kinetic energy can be several volts at small R values, and the p -wave phase shift can be non-negligible. Accordingly, if $l_0=1$ (or higher partial waves) are important, they are easily handled in first-order perturbation theory.⁸ This amounts to simply adding the following correction to the right-hand side of Eq. (8):

$$\Delta \bar{K}_{ll'} = \frac{6\pi}{k^3} \tan \delta_{l_0-1} \{ \nabla [F_l(r) Y_{l\lambda}^*(\hat{r})] \cdot \nabla [F_{l'}(r) Y_{l'\lambda}(\hat{r})] \}_{\mathbf{r}=\mathbf{R}} \quad (15)$$

It should also be pointed out that whenever $R > -1/\varepsilon(R)$, the value of k becomes imaginary, since $T_e < 0$. This causes some difficulty, since the e - B scattering phase shifts are normally available only at positive energies. But since $k^{-1} \tan \delta_{l_0=0}$ is smooth near $T_e=0$ it can be simply extrapolated to (or calculated *ab initio* at) negative energies. It should be stressed that high accuracy is not needed in this extrapolation, since each potential curve rapidly approaches its asymptotic atomic limit in this region anyway. The behavior of the p -wave correction (15) is slightly more problematic, since $k^{-2l_0-1} \tan \delta_{l_0}$ diverges as $T_e \rightarrow 0$ for $l_0 \geq 1$ because of the long-range polarization field.⁹ This divergent piece is appreciable only in the immediate vicinity of $k=0$ [i.e., where $R = -1/\varepsilon(R)$], and it can in practice be simply subtracted. The localized divergence is clearly unphysical since it stems from the most distant long-range contributions to the phase shift, whereas the actual electronic wave function decays exponentially at large distances.

Figure 1(a) compares some of the resulting ($\lambda=0$) CsHe potential curves with Pascale's variational pseudopotential calculation, the best results obtained to date for this dimer. Note the correct representation of many critical features, especially the two avoided crossings between $5d\sigma$ and $7s\sigma$ and between $7p\sigma$ and $6d\sigma$. The avoided crossing between $5d\sigma$ and $7s\sigma$ is apparently particularly sensitive; it did not show up in the first (l -independent) pseudopotential calculations, but its existence has been experimentally confirmed (see Fig. 1 of Dubourg, Ferray, Visticot, and Sayer⁴). [We also find that this crossing disappears if the first-order Born approximation is used in place of Eqs. (8) and (11).] The potential curves of

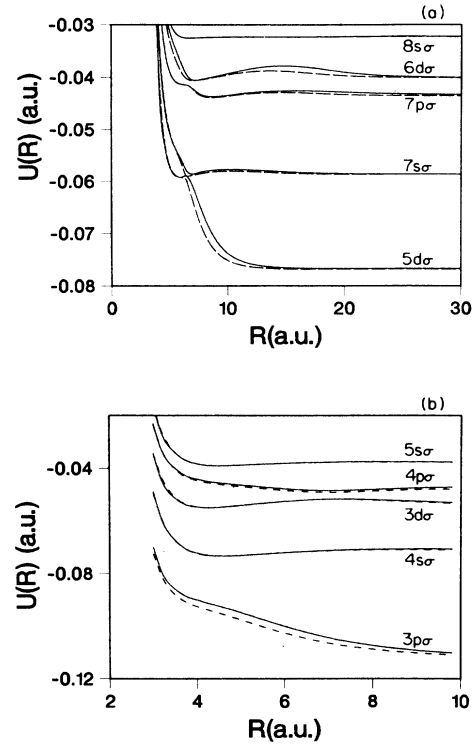


FIG. 1. Several Born-Oppenheimer potential curves resulting from our nonperturbative Fermi-type analysis (dashed curves) are compared to the best calculations of Pascale (smooth curves, from Ref. 2) for (a) CsHe and (b) NaHe. The curves shown include the potential for the alkali-ion-rare-gas system in addition to the energy $\varepsilon(R)$ of the valence electron.

NaHe, shown in Fig. 1(b), are also informative. The calculations of Ref. 2 (l -dependent pseudopotential) and of Ref. 10 (l -independent model potential) agree with each other and with our results reasonably well. Similar comparisons have been obtained for other alkali-rare-gas dimers.

The good agreement between elaborate potential curve calculations and this nonperturbative Fermi-type analysis suggests that two-body scattering properties can in fact be used to determine major features of the composite system. By expressing final results in terms of a body-frame reaction matrix $K_{ll'}(R)$, this treatment provides an immediate link to quantum-defect formulations,⁶ thereby permitting a straightforward description of non-Born-Oppenheimer processes such as predissociation, l -changing collisions, and Penning ionization. This procedure outlined above can also be generalized without much difficulty to deal with a *multichannel* Rydberg atom (e.g., barium) which is perturbed by a rare-gas atom. The extension to handle *several* perturbing atoms simultaneously also appears to be clear-cut, and may prove useful for studying Rydberg states of clusters. On the other hand, treatment of *open-shell* perturbing atoms appears somewhat more difficult than the above description of rare-gas perturbers, and will require further development.

To date, numerous efforts to extend Fermi's treatment have been made (see, e.g., Refs. 3, 7, 9, and 11). The most relevant is the recent work of de Prunele,⁷ which also determines the alkali-metal-rare-gas potential curves from the atomic quantum defects and the e - B scattering information. The theoretical formulation of de Prunele is substantially different, however, since in Ref. 7 the "smooth" Coulomb Green's function⁶ is not used, and accordingly a "smooth" reaction matrix is not obtained. In our multichannel quantum defect theory treatment, the reaction matrix varies smoothly with energy (even across threshold), and it embodies all the information of channel interactions. Consequently, the calculation can be performed on a coarse energy mesh. By linking more directly

to quantum-defect theory, processes such as dissociative recombination can also be treated using the K matrix obtained by the present method. Nevertheless, Ref. 7 has obtained results which seem very close to ours, and the two treatments should enjoy a comparable advantage over conventional calculations in simplicity and in ease of computation.

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