Molecular Rydberg Transitions. X
Correlation Algorithms for Rydberg Term Values *

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The empirical linear correlations of Rydberg term values [S. P. McGlynn, S. Chattopadhyay, P. Hochmann, and H.-t. Wang**, are discussed in a first-order perturbation-theoretic format. In the second-order, quadratic dependencies are expected. The theoretical development assumes that the gross features of interatomic and intermolecular Rydberg term value variations can be discerned using a one-electron model; that a molecule XS, X being the Rydberg chromophore and S the substituent, can be partitioned so that the affairs of the optical electron are dominated by its interactions with the chromophoric segment; and that the charge distributions, whether of X or S, can be expanded in ways which permit evaluation of the effects of small variations in either X or S on Rydberg term values. The development is restricted to Class 1 molecules: Molecules which possess a common S and variable X, but where all X must be of similar electronic structure e.g., X = F, *Cl*, Br, I). A variety of correlative algorithms is discussed, and the intergroup transferability of parameters is elaborated in terms of the properties of "average chromophores".

1. Introduction

A) Prefatory Comments

The assignment of Rydberg states and series is a complicated affair which is fraught with much uncertainty. The various procedures, ambiguous though they be for atoms, become more tenuous in molecules because of:

(i) The existence of vibrational excitations, which not only decrease definition by increasing the density of states, but also cause large perturbations of individual series members via vibronic coupling.

(ii) The increased density of ionization limits, which also, via the increased density of Rydberg states, leads to severe inter-channel interactions.

(iii) The existence of intravalence excitations which, by coupling with Rydberg transitions, cause the latter to lose their Rydberg character and make them indistinguishable from the former.

The net result is that molecular Rydberg series are often fragmentary and that the surviving members are sometimes indistinguishable from intravalence excitations. Thus, in molecules, the assignment process becomes especially difficult and any tactic which provides either help or insight acquires a crucial importance.

Recent empirical evidences suggest that Rydberg excitation energies are linear functions of the ionization energy [1–4]. This observation, which implies an effective inversion of the Rydberg equation [5] and its conversion from a correlative algorithm of *intra*molecular nature to one of *inter*molecular character, will, if correct, provide an important assignment tactic in molecular spectroscopy. Validation of the generality of these observations [1–4] can progress in two ways. It can be shown, for example, that the observed linearities rest on sound theoretical grounds. Unfortunately, the existing efforts along these lines are meager [6] and, while interesting, they do not constitute a very strong basis for linear behavior. The second way consists of continued (brute force) empirical justification and, indeed, efforts along these lines have been multiplying. McGlynn, et al. [1] have established a predictive ability of $\sim 100\ \mathrm{cm}^{-1}$ for various Rydberg states of hydrogen halides. These limits, accurate

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though they be, have actually been surpassed by Fock, Gürtler, and Koch [7] in their VUV studies of BF, CO and N_2. Finally, Spence [8] has been eminently successful in applying these same tactics to Feschbach resonances in rare gases, hydrogen halides and methyl halides. One may conclude, then, that the empirical basis is sound.

The present work is an effort to construct a theoretical basis from which the linear correlational algorithms will emerge. It is, however, a zero-order effort, in that the formalism is purposely developed only at the one-electron level. The restriction to the one-electron level is justified as follows: Firstly, concepts pertinent to polyatomic molecules, concepts which are non-utilitarian or non-existent for atoms, must be developed. Among those, for example, we list the concepts of chromophore, substituent, partitioning of charge density, etc. These concepts are easily developed in one-electron format and, fortunately, their meaning in the many-electron format suffers no great alteration. Secondly, the processing at the one-electron level will serve to point out those characteristics which demand a many-electron approach and those which do not. In this way, the physics acquires clarity, since it implies a knowledge of the transference of specifically many-electron effects from the theoretical to the empirical plane.

Within the context of the one-electron scheme and at various levels of perturbation theory, the various correlation algorithms which can exist between different Rydberg term values will be developed. It will be shown that one of these is linear, and discussion at a many-electron level will assuredly change its form and meaning but little, if at all. However, without making the apparently catastrophic assertion that the ionization potential of a molecule (or atom) is, in fact, its largest term value (within the context of some particular Rydberg series), the observed term value/ionization limit linearity may not be justified. We do not view this as a disturbing state of affairs. Rather, we think it useful to know what can and cannot be done within set limits and, even more so, to know the deterrents which play the inhibitory theoretical roles. Thus, this work serves as the necessary introduction to a many-electron approach and to a correlative work on ionization potentials (which takes the view that ionization potentials are indeed lowest term values) which the present authors are preparing.

B) *Definitions and Assertions*

The term values of Rydberg states correlate linearly with the corresponding ionization potentials [1]. The form of the correlation is

$$T(\mu, \tilde{\alpha}, n) = a_{\alpha n} I_\mu + b_{\alpha n} . \tag{1.1}$$

The symbol $T(\mu, \tilde{\alpha}, n)$ denotes the actual term value of the nth lowest-energy Rydberg state of α type and is to be distinguished from $T(\mu, \alpha, n)$ which, with respect to a Hamiltonian to be defined later (*vide infra*), is the *theoretical* one-electron component of $T(\mu, \tilde{\alpha}, n)$; α is a symmetry label or some other appropriate designation for the Rydberg state in question; and μ denotes the cationic core on which the states $(\mu, \tilde{\alpha}, n)$, n variable, converge as $n \to \infty'$. The ionization potential I_μ is the energy difference between the μth cationic state and the ground state of the neutral species. In line with the definition of $T(\mu, \tilde{\alpha}, n)$, the subscript α in the slopes $a_{\alpha n}$ and in the intercepts $b_{\alpha n}$ designates the symmetry representation of the virtual orbital which, within the one-electron picture, is the terminal orbital of the Rydberg absorption process.

Identical correlations, of the form [see Eq. (4.9)]

$$T(\mu, \tilde{\alpha}, n) = a\, T(\nu, \tilde{\beta}, m) + b , \tag{1.2}$$

where $(\mu, \tilde{\alpha}, n)$ and $(\nu, \tilde{\beta}, m)$ denote different core/Rydberg states, also exist. They differ from those of Eq. (1.1) only in that an ionization potential is replaced by a Rydberg term value; and that, as expected, they are of considerably higher fidelity.

Equations (1.1) and (1.2) are used in an *inter*atomic (or *inter*molecular) fashion [1—4] as opposed to the *intra*atomic (or *intra*molecular) processing of the Rydberg equation [5]. These correlations were deduced empirically and are not understood [6]. Furthermore, they are valid only within certain groups of atoms and molecules. These groups, if atomic, lie within columns of the periodic table; and, if molecular, contain fixed substituents (or chromophores), where all substituents (or chromophores) possess a similar valence-electronic structure [1, 9].

The least-squares values of the parameters a and b display regular *intra*group behavior, and exhibit variations from one group to another which are also regular [1]. It is reasonable to expect that the empirical values of a and b should contain information about the interactions of the excited optical electron with the atomic and/or molecular cores. It is also probable that some components of these parameters are *inter*-group transferable. Consequently, it is necessary to inquire whether the above correlations can be generalized so that the definition of a group, whether of atoms or of molecules, can be made less stringent.

The primary purpose of this work is to interpret Eq. (1.2) in a one-electron model and, in so doing, to generate a perturbation-theoretic hierarchy of correlation algorithms. Moreover, we view this study as a necessary preliminary to an interpretation of Eq. (1.1) — an interpretation which must be based on a more elaborate Hamiltonian than the one utilized for the present model. In this paper, however, we do not refrain from pointing out insights which result from our discussion of Eq. (1.2) and which may be of importance to a future treatment of Equation (1.1).

In formulating our model, we emphasize empirically parametrizable interatomic and intermolecular relations between Rydberg term values, and we de-emphasize computational schemes. Therefore, the model reflects those features of Rydberg excited states which we consider critical. The major assumptions of the model are:

A1) The gross interatomic and intermolecular variations of Rydberg term values are assumed to be reflected in a one-electron model. The appropriate one-electron Hamiltonian, then, need only account for the Coulomb interactions [10] of the optical electron with a rigid atomic or molecular core. The core charge density can be identified as that of the μth parental cationic state.

A2) A molecule XS is partitioned into two parts: A substituent part S and a Rydberg chromophoric part X. (In methyliodide, CH_3I, for example, $S = CH_3$ and $X = I$.) The term values are assumed to be dominated by the interaction of the optical electron with the chromophoric segment X, while the substituent segment S is assumed to produce effects of secondary importance. Consequently, the core charge distribution, and the core potential to which it gives rise, can be divided into a chromophoric part and a substituent part. (A2 is required only for molecules.)

A3) The charge distributions, whether associated with the chromophoric or substituent parts of the core, are assumed to be expandable in ways which reflect the major variations of the core potential caused by changes in the structure of the chromophore and/or the substituent. The possibility of such an expansion is confined, at least initially, to atomic (or molecular) species which belong to the same group. (Only part of A3 is required for an atomic group.)

A1 stems from fairly common ideas about the nonbonding nature (i.e., loosely bound character) or Rydberg virtual orbitals [5, 11, 12] and, in particular, from a (naive) approximation stressing the relative unimportance of exchange and spin orbital interactions between the core and the Rydberg orbital [10—13]. A2 is predicated on the existence of regular trends in the intermolecular variations of term values. Many such regular trends have been observed [1—4, 14]. A3, which embraces atomic as well as molecular groups, is based on the same premises as A2 but, being a standard theoretical ploy, is more readily accepted.

The first- and second-order solutions of the Hamiltonian eigenequation which is constructed within the set of assumptions A1—3 yield a variety of correlative algorithms for Rydberg term values. We shall emphasize the intermolecular aspects of these solutions since, then, the interatomic aspects become merely a special case (i.e., the case which arises when the molecule XS possesses no substituent and X is atomic). We further limit ourselves to the class of molecules XS where X is variable and S is fixed.

Finally, within the theoretical *ansatz* presented, we provide justification for the introduction of the concept of an "average chromophore" [1, 2], and we rationalize the utility of a serial indexing of Rydberg states as opposed to an *aufbau* labelling [1—3].

Throughout, the index n (or m) is a simple serial index whose values are denoted $1', 2', 3', \ldots$, corresponding to 1*st* Rydberg, 2*nd* Rydberg, 3*rd* Rydberg, etc. The *aufbau* principal quantum number is denoted n^0 (or m^0), and its values are given as $1, 2, 3, \ldots$.

2. Partitioning of the Core Hamiltonian Into Chromophore and Substituent Parts

We shall now develop a one-electron Hamiltonian which has embedded in it the suppositions A1—3 of the previous Section.

We denote by $T(\mathrm{XS}, \mu, \alpha, n)$ the one-electron component of the term value $T(\mathrm{XS}, \mu, \tilde{\alpha}, n)$ of a Rydberg excited state of the species XS. Thus, $-T(\mathrm{XS}, \mu, \alpha, n)$ is a discrete eigenvalue of the one-electron, spinless Hamiltonian $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$:

$$\{\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu) + T(\mathrm{XS}, \mu, \alpha, n)\} \cdot \varphi(\boldsymbol{r}; \mathrm{XS}, \mu, \alpha, n) = 0, \quad (2.1)$$

where φ represents the orbital which is terminal to the Rydberg excitation in question. The Hamiltonian $\hat{H}$, which is more precisely defined in Appendix A, takes account only of the Coulomb interactions between the rigid core XS^+ and the optical electron.

As shown in Appendix B, the core electrostatic potential $V(\boldsymbol{r}; \mathrm{XS}, \mu)$ may be partitioned into an X-component, $V(\boldsymbol{r}; \mathrm{X/S}, \mu)$, and an S-component, $V(\boldsymbol{r}; \mathrm{S/X}, \mu)$. Further,

$$\lim_{r \to \infty} r\, V(\boldsymbol{r}; \mathrm{X/S}, \mu) = Z e^2,$$
$$\lim_{r \to \infty} r\, V(\boldsymbol{r}; \mathrm{S/X}, \mu) = 0. \quad (2.2)$$

Such asymptotic behavior, combined with the assumption (A1) that the amplitude of a Rydberg orbital inside and near the core is small, constitutes a basis for the argument that the leading terms of $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$ are contained in the chromophoric part of the core potential. Therefore, we write

$$\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu) = \hat{H}(\boldsymbol{r}; \mathrm{X/S}, \mu) + V(\boldsymbol{r}; S/X, \mu),$$
$$\hat{H}(\boldsymbol{r}; \mathrm{X/S}, \mu) = -(\hbar^2/2m)\Delta + V(\boldsymbol{r}; \mathrm{X/S}, \mu). \quad (2.3)$$

Further development of $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$ is based on the continued application of the assumption (A2) that, within the perturbation treatment of Eq. (2.1), the Hamiltonian $\hat{H}(\boldsymbol{r}; \mathrm{X/S}, \mu)$ contains zero, first- and higher-order terms while $V(\boldsymbol{r}; \mathrm{S/X}, \mu)$ contains first- and higher-order terms only.

The variety of empirical intermolecular correlations obtained for Rydberg term values [1—4, 14], as well as preliminary theoretical results [6], suggests that the perturbation expansion of the Hamiltonian of Eq. (2.3), and its subsequent semiempirical parametrization, should be particularly tractable when the various species XS can be arranged into two classes:

Class 1. The group possesses a common substituent S and a variable chromophore X. All chromophores X within the group must also possess a similar valence-electronic structure (e.g., —F, —Cl, —Br, —I).

Class 2. The group possesses a common chromophore X and variable substituent S. All substituents S within the group must also possess a similar valence-electronic structure (e.g., $\mathrm{CH_3}$—, $\mathrm{C_2H_5}$—, $\mathrm{C_3H_7}$—, etc.).

As mentioned in Section 1, we shall develop the Hamiltonian of Eq. (2.3) along lines suitable for correlations of Class 1, including interatomic correlations. Correlative relations for Class 2 molecular groups will be discussed elsewhere [9].

3. Perturbation Expansion of the Hamiltonian $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$

We now effect a separation of the zero-, first- and higher-order terms from the Hamiltonian of Equation (2.3). In doing so, we accept guidance from the empirical behavior of the correlations of Eqs. (1.1) and (1.2). Equation (1.1) is rewritten as

$$T(\mu, \tilde{\alpha}, n) = a_{\alpha n}(I_\mu - \bar{I}_\mu) + (b_{\alpha n} + a_{\alpha n} \bar{I}_\mu), \quad (3.1)$$

where $\bar{I}_\mu$ is some average of the ionization potentials I_μ within the group XS which is of interest [15].

Equation (3.1) emphasizes the fact that the term values $T(\mu, \tilde{\alpha}, n)$ vary about an average value, $b_{\alpha n} + a_{\alpha n} \bar{I}_\mu$. Since the slopes $a_{\alpha n}$ are relatively small (i.e., $|a_{\alpha n}| \leq 0.1$), the variable part of the term values, $a_{\alpha n}(I_\mu - \bar{I}_\mu)$, is much smaller than the average, $b_{\alpha n} + a_{\alpha n} \bar{I}_\mu$. Hence, in the case of correlations of Class 1, it is plausible to introduce the concept of an "average chromophore" $\bar{\mathrm{X}}$ and to interpret the intercepts of Eq. (3.1) as the electrostatic component of the term values of an hypothetical species $\bar{\mathrm{X}}\mathrm{S}$. In this context, $\bar{I}_\mu$ must then correspond to the μth ionization limit of $\bar{\mathrm{X}}\mathrm{S}$ and the slopes $a_{\alpha n}$ must reflect deviations of the charge densities of the individual chromophores X from that of $\bar{\mathrm{X}}$.

The empirical behavior [1] of $a_{\alpha n}$ and $b_{\alpha n}$ shows clearly that the change of substituent has a significant effect only on the intercepts $b_{\alpha n}$. From this we infer that the dependence of the chromophoric electron density on S is not very strong and that it may be disregarded within the first-order perturbation. Similarly, we infer that the dependence of the substituent electron density on individual chromophores X is also quite weak and that, within first-order perturbation limits, it may be replaced by that for the average chromophore $\bar{X}$.

Finally, the observation of rapid decrease of $|a_{\alpha n}|$ with increasing n and the increasing conformity of the intercepts $b_{\alpha n} + a_{\alpha n} I_\mu$ (again with increasing n) with the Rydberg term formula suggests that it might be advantageous to separate out the electric monopole component of the chromophoric charge density from the higher multipole parts.

When the above *ansatz* is processed (see Appendix C for details), the prescribed perturbation expansion of the Hamiltonian is found to be

$$\begin{aligned}\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu) = \hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu) &+ (N_\mathrm{X} - \bar{N}) v_{10}(\boldsymbol{r}) \\ &+ (Z-1) v_{01}(\boldsymbol{r}) + v_\mathrm{S}(\boldsymbol{r}) \\ &+ (N_\mathrm{X} - \bar{N})^2 v_{20}(\boldsymbol{r}) \\ &+ (N_\mathrm{X} - \bar{N})(Z-1) v_{11}(\boldsymbol{r}) \\ &+ (Z-1)^2 v_{02}(\boldsymbol{r}) + \cdots, \end{aligned} \quad (3.2)$$

where $N = N_\mathrm{X} + N_\mathrm{S}$ represents the electron partitioning of XS (see Appendic B); where $\bar{N}$ is the average value of N_X (see Appendix C); where $\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu)$, the zero-order part of $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$, is defined as

$$\begin{aligned}\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu) = &-\frac{\hbar^2}{2m}\Delta - \frac{Z}{r} \\ &+ \bar{N} \int \mathrm{d}\boldsymbol{r}' \, |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \{\Gamma_{00}(\boldsymbol{r}') - \delta(\boldsymbol{r}')\};\end{aligned} \quad (3.3)$$

and where $\Gamma_{00}(\boldsymbol{r}')$ represents the first component in a power series expansion of the spinless electron density $\Gamma(\boldsymbol{r}')$ (see Appendix C). The Hamiltonian of Eq. (3.3) determines the Rydberg term values and orbitals of the average chromophore $\bar{\mathrm{X}}$ with net charge Z.

The second and third terms of Eq. (3.2) represent contributions to the core potential due to variations of the chromophoric electron density — variations which, within the group of correlated molecules XS, are linear in both N_X and Z. The fourth term is the potential generated by the substituent charge density of the average species $\bar{\mathrm{X}}\mathrm{S}^+$. (The potentials v_{10}, v_{01} and v_S are defined in Appendix C.) These three terms constitute the first-order corrections to the Hamiltonian $\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu)$.

The last three terms of Eq. (3.2) are the contributions to the core potential from variations of the chromophoric electron density which are quadratic in N_X and Z. (The potentials v_{20}, v_{11} and v_{02} are defined in Appendix C.) These three terms constitute the second-order corrections to $\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu)$.

4. Intermolecular and Interatomic Variations of Rydberg Term Values

We now show, for the group of related species XS, that the first-order estimates of $T(\mathrm{XS}, \mu, \alpha, n)$ are linearly dependent on the first-order estimates of $T(\mathrm{XS}, \nu, \beta, m)$. The second-order estimates will be shown to yield a quadratic dependence of $T(\mathrm{XS}, \mu, \alpha, n)$ on $T(\mathrm{XS}, \nu, \beta, m)$.

A) Zero-, First-, and Second-Order Eigenvalues of the Hamiltonian $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$

The zero-order eigenvalues and eigenfunctions of Eq. (2.1) are given by

$$\{\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu) + T(\bar{\mathrm{X}}, \mu, \alpha, n)\} \cdot \varphi(\boldsymbol{r}; \bar{\mathrm{X}}, \mu, \alpha, n) = 0, \quad (4.1)$$

where $\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu)$ is defined in Equations (3.3). We now abbreviate the zero-order term value

$$T(\bar{\mathrm{X}}, \mu, \alpha, n) \quad \text{to} \quad T_0(\mu, \alpha, n);$$

the zero-order Rydberg orbital $\varphi(\boldsymbol{r}; \bar{\mathrm{X}}, \mu, \alpha, n)$ to $|\mu, \alpha, n\rangle$; and the first- and second-order eigenvalues of the Hamiltonian of Eq. (3.2) to $T_1(\mu, \alpha, n)$ and $T_2(\mu, \alpha, n)$, respectively.

Assuming that $-T_0(\mu, \alpha, n)$ is a non-degenerate eigenvalue of $\hat{H}(\boldsymbol{r}; \bar{\mathrm{X}}, \mu)$, we have

$$\begin{aligned}&T_1(\mu, \alpha, n) - T_0(\mu, \alpha, n) \\ &= Q_{10}(\mu, \alpha, n) + (N_\mathrm{X} - \bar{N}) Q_{11}(\mu, \alpha, n),\end{aligned} \quad (4.2)$$

where the coefficients $Q_{10}(\mu, \alpha, n)$ and $Q_{11}(\mu, \alpha, n)$ are defined as

$$\begin{aligned}&Q_{10}(\mu, \alpha, n) \\ &= -\langle \mu, \alpha, n | v_\mathrm{S} + (Z-1) v_{01} | \mu, \alpha, n \rangle, \\ &Q_{11}(\mu, \alpha, n) = -\langle \mu, \alpha, n | v_{10} | \mu, \alpha, n \rangle.\end{aligned} \quad (4.3)$$

For the second-order estimate, $T_2(\mu, \alpha, n)$, we find

$$\begin{aligned}&T_2(\mu, \alpha, n) - T_0(\mu, \alpha, n) \\ &= Q_{20}(\mu, \alpha, n) + (N_\mathrm{X} - \bar{N}) Q_{21}(\mu, \alpha, n) \\ &\quad + (N_\mathrm{X} - \bar{N})^2 Q_{22}(\mu, \alpha, n).\end{aligned} \quad (4.4)$$

Providing that the only second-order terms of $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$ which are considered are those pertaining to the potentials v_{10}, v_{01} and v_S of Eq. (3.2), the coefficients of Eq. (4.4) are given by

$$\begin{aligned}
Q_{20}(\mu,\alpha,n) = {} & -\langle\mu,\alpha,n|\,[v_{\mathrm{S}} + v_{\mathrm{S}}\hat{\Sigma}v_{\mathrm{S}}] + (Z-1)\,[v_{01} + v_{01}\hat{\Sigma}v_{\mathrm{S}} + v_{\mathrm{S}}\hat{\Sigma}v_{01}] \\
& + (Z-1)^2\,[v_{02} + v_{01}\Sigma v_{01}]\,|\mu,\alpha,n\rangle\,, \\
Q_{21}(\mu,\alpha,n) = {} & -\langle\mu,\alpha,n|\,[v_{10} + v_{10}\hat{\Sigma}v_{\mathrm{S}} + v_{\mathrm{S}}\hat{\Sigma}v_{10}] + (Z-1)\,[v_{11} + v_{01}\hat{\Sigma}v_{10} + v_{10}\hat{\Sigma}v_{01}]\,|\mu,\alpha,n\rangle\,, \\
Q_{22}(\mu,\alpha,n) = {} & -\langle\mu,\alpha,n|\,v_{20} + v_{10}\hat{\Sigma}v_{10}\,|\mu,\alpha,n\rangle\,,
\end{aligned} \tag{4.5}$$

where the symbol Σ denotes the selection operator [16]

$$\hat{\Sigma} \equiv \sum_{\substack{\delta \neq \alpha \\ k \neq n}} |\mu,\delta,k\rangle\langle\mu,\delta,k|/[T_0(\mu,\alpha,n)]\,.$$

B) *First- and Second-Order Relationships between One-Electron Components of the Rydberg Term Values*

We consider two manifolds of Rydberg states which, within the approximations set forth here, may be characterized by indices μ, α, n and ν, β, m for all species XS of the group of related molecules. Combining Eqs. (4.2), one for each of the two sets of indices, we can eliminate the variable $N_{\mathrm{X}} - \bar{N}$. As a result, we obtain a linear relation between the variations of the first-order estimates of the Rydberg term values around the corresponding zero-order estimates. This relation is

$$\begin{aligned}
T_1(\mu,\alpha,n) - T_0(\mu,\alpha,n) = {} & K_{10}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& + K_{11}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix}[T_1(\nu,\beta,m) - T_0(\nu,\beta,m)]\,.
\end{aligned} \tag{4.6}$$

The coefficients K_{10} and K_{11} of Eq. (4.6) may be expressed in terms of the coefficients Q_{10} and Q_{11} of Eq. (4.3) as

$$\begin{aligned}
K_{11}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} &= Q_{11}(\mu,\alpha,n)/Q_{11}(\nu,\beta,m)\,, \\
K_{10}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} &= Q_{10}(\mu,\alpha,n) \\
& \quad - Q_{10}(\nu,\beta,m)K_{11}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix}.
\end{aligned} \tag{4.7}$$

The variable $N_{\mathrm{X}} - \bar{N}$ may also be eliminated from Eqs. (4.4), one equation for each of the two manifolds μ, α, n and ν, β, m of Rydberg states. The neglect of all terms which accompany cubic- and higher-orders of the perturbational ordering parameter, yields

$$\begin{aligned}
T_2(\mu,\alpha,n) - T_0(\mu,\alpha,n) = {} & K_{20}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& + K_{21}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix}[T_2(\nu,\beta,m) - T_0(\nu,\beta,m)] \\
& + K_{22}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix}[T_2(\nu,\beta,m) - T_0(\nu,\beta,m)]^2\,.
\end{aligned} \tag{4.8}$$

Expressions for the coefficients K_{20}, K_{21} and K_{22} of Eq. (4.8) are given in terms of the coefficients Q_{20}, Q_{21} and Q_{22} in Appendix D.

Equation (4.6) can be transformed into a form suitable for comparison with experimental term values:

$$\begin{aligned}
T_1(\mathrm{XS},\mu,\alpha,n) = {} & a_1\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& + b_1\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} T_1(\mathrm{XS},\nu,\beta,m)\,,
\end{aligned} \tag{4.9}$$

where the slope b_1 is identical to K_{11} of Eq. (4.6) and the intercept a_1 is given by:

$$\begin{aligned}
a_1\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} = {} & T(\bar{\mathrm{X}},\mu,\alpha,n) + K_{10}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& - K_{11}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} T(\bar{\mathrm{X}},\nu,\beta,m)\,.
\end{aligned} \tag{4.10}$$

The symbols XS and $\bar{\mathrm{X}}$ have been re-introduced in Eqs. (4.9) and (4.10) in order to emphasize the intermolecular (or interatomic) content of the relations.

Similarly, Eq. (4.8) may be transformed into

$$\begin{aligned}
T_2(\mathrm{XS},\mu,\alpha,n) = {} & a_2\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} + b_2\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& \cdot T_2(\mathrm{XS},\nu,\beta,m) + c_2\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} T_2(\mathrm{XS},\nu,\beta,m)^2\,,
\end{aligned} \tag{4.11}$$

where the coefficient c_2 is identical to K_{22} of Eq. (4.8) and the coefficients b_2 and a_2 are given by

$$\begin{aligned}
b_2\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} = {} & K_{21}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& - 2K_{22}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} T(\bar{\mathrm{X}},\nu,\beta,m)\,, \\
a_2\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} = {} & T(\bar{\mathrm{X}},\mu,\alpha,n) + K_{20}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} \\
& - K_{21}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} T(\bar{\mathrm{X}},\nu,\beta,m) \\
& + K_{22}\begin{pmatrix}\mu & \alpha & n\\ \nu & \beta & m\end{pmatrix} T(\bar{\mathrm{X}},\nu,\beta,m)^2\,.
\end{aligned} \tag{4.12}$$

5. Discussion

A comparison of the relations (4.6, 8) or (4.9, 11) with the experimental term values can be done in a number of different ways. The approach which we pursue here is aimed at the generation of empirical relations such as Equation (1.2).

A) *Equations* (4.9) *and* (4.11) *as Correlative Algorithms*

Since the coefficients a, b and c of Eqs. (4.9, 11) relate to matrix elements of the Hamiltonian of Eq. (3.2), it should be possible to devise a suitable semi-empirical computational scheme and, hence, compute them. The pseudo-potential technique of Rice [17] and McKoy [18] appears to be particularly appropriate for an initial effort. Such computations will no doubt yield a quite critical test of the assumptions and approximations made in this article. However, our primary goal is the inference of correlative relations capable of reproducing the gross intermolecular and interatomic variations of Rydberg term values. Therefore, we treat the coefficients of Eq. (4.9) and Eq. (4.11) as adjustable parameters whose values will be determined from experimental term values by means of a suitable optimization procedure.

There are two ways in which the experimental term energies may be used as input for Equations (4.9, 11). First, we may evaluate the *one-electron* components of the term values from the *experimental* term energies. This has been done [1] using expressions which relate the energy levels of a given orbital configuration to Coulombic, exchange, spin-orbital and other interactions [11, 12]. Unfortunately, for many atomic and virtually all molecular configurations, appropriate expressions do not exist. Moreover, the extraction of the *one-electron* energy requires data for all (or nearly all) energy levels of the configuration of interest. While such data are abundant for lower-energy excited atomic states, they are very scarce for high-energy atomic states [1, 2] and for almost all molecular excited states [1].

The second alternative, required only when the data base is inadequate or the coupling matrices are too complicated, assumes that the Rydberg level separations which arise from a given Rydberg configuration are small in comparison with the overall variations of term values which occur in the XS group [14]. This assumption, fortunately, is subject to verification in any given instance. If correct, it follows that the experimental term energies will exhibit the linear dependencies of Eq. (4.9) (or the quadratic dependencies of Eq. (4.11) when the second-order corrections become significant). And, upon completion, the plausibility of the approximation may be rechecked using the statistical significance of the empirical correlations (if any) that are found.

The study of interatomic or intermolecular variations of term values via correlations of the unprocessed experimental term energies does not require a full knowledge of the complete manifold of energy levels [1]. Indeed, in many instances, the correlative approach does not require an exact identification of individual levels or even their configurational parentage (i.e., of the indexes μ, α or n). Such reasons, we think, constitute a powerful argument for empirical correlative approaches guided by the qualitative form of Eqs. (4.9, 11). This point is elaborated below.

B) *Selection of the Input Data Sets for Term Value Correlations*

In order to evaluate the correlations suggested by Eqs. (4.9, 11), the terms whose energies serve as input must be selected. Such a sampling procedure involves two steps.

First, the atoms and/or molecules must be assembled into related groups. In the empirical approach, as outlined in the preceding Section, the selection of "structurally homogeneous" populations of atomic and/or molecular species is a rather intuitive, trial-and-error procedure. However, a useful guide is provided by the qualitative dependencies of the coefficients of Eqs. (4.9, 11) on the substituent, on the net core charge and on the index n (this point is discussed in the next Section). Ultimately, the propriety of any grouping will be determined by the statistical significance of the correlations obtained.

Second, for a given group, we must select the term manifolds $\{\mu, \alpha, n\}$ and $\{\nu, \beta, m\}$ which are to be associated with the core/Rydberg orbital configurations (μ, α, n) and (ν, β, m), respectively. The identification of the μth and the νth parental cores and the assignment of the symmetry types α and β of the Rydberg orbitals must be inferred from spectroscopic data. The requirement that the indexes μ, α and ν, β must be the same for every entity from the group XS provides, in many instances, a guide for the selection of such groups. These indexes must also remain constant for all terms from the manifolds $\{\mu, \alpha, n\}$ and $\{\nu, \beta, m\}$. At this point, the relationship between the serial numbers n or m and the *aufbau* principal quantum numbers, n^0 or m^0, must be clarified.

According to Eq. (2.1), n denotes the nth lowest-energy eigenstate belonging to the αth representation of the symmetry group of the Hamiltonian $\hat{H}(\boldsymbol{r};\, \mathrm{XS},\, \mu)$. As shown in Appendix A, we do not assume any particular expansion of the core wavefunctions in terms of the set of one-electron states — an approach which is fundamental to the *aufbau* designation. Therefore, no general, simple relationship between the index n and the *aufbau* principal quantum number n^0 should be expected. Nevertheless, in some simple cases, such a relation can be established. In the case of atomic species with a closed-shell ground state, for example, we can identify the eigenstates (μ, α, n) of $\hat{H}(\boldsymbol{r};\, \mathrm{XS},\, \mu)$ with the *aufbau* one-electron states which, in a formal sense, are not occupied in the ground state configuration. Denoting the principal quantum number of the highest-energy, ground-state occupied, *aufbau* orbital of the αth symmetry type by $n^0(\alpha)$, and that of the Rydberg orbital by $n^{0\prime}(\alpha)$, the indexes n and n^0 are related as $n = n^{0\prime}(\alpha) - n^0(\alpha)$. This correspondence implies that atomic transitions which, within the *afbauu* labelling scheme, are classified as *intra*shell (i.e., $\Delta n^0 = 0$) or infrashell (i.e., $\Delta n^0 \leqq -1$), will now be treated as Rydberg transitions (i.e., $\Delta n \geqq 1$).

For closed-shell molecules, the situation is considerably more complex. It is necessary to differentiate between molecular Rydberg orbitals and molecular valence orbitals, the latter being terminal to a variety of valence excitation processes. Since the difference between Rydberg and valence orbitals is gauged by the extent of the differential overlap between the orbital and the molecular core, rather than by relative energy or by orbital symmetry, the *aufbau* assignment does not aid in the selection of Rydberg transitions. Moreover, for larger molecules of low symmetry, the *aufbau* indices are ambiguous since, oftentimes, they are entirely dependent on the computational procedure by which the orbitals were generated.

The designation of one-electron Rydberg states by the index n is neither more confusing nor more difficult than the conventional *aufbau* labelling, and it does offer several advantages. First, it assigns the same index to all correlated terms even when the chromophores contain atoms from different rows of the periodic table. Second, the partitioning of effective quantum numbers into the index n and the quantum defect yields quantum-defect values which are nearly independent of the chromophore. Third, a comparison of n-labelled Rydberg states of known molecules/atoms to those of newly-studied molecules/atoms provides a simple means for spectroscopic assignment [19].

The manifold of term values $\{\nu, \beta, m\}$ plays the role of an independent variable with respect to correlations with other manifolds $\{\mu, \alpha, n\}$. When a physically relevant mapping of the $\{\mu, \alpha, n\}$ manifold onto the $\{\nu, \beta, m\}$ manifold has been established, this mapping may be evaluated by means of standard optimization procedures (such as the least-squares technique). Such mappings may also be inferred from symmetry considerations and coupling schemes. The most primitive example of a mapping is that between the manifolds $\{\mu, \alpha, m\}$ and $\{\mu, \alpha, n\}$, $m \neq n$, and such is the topic of the next Section.

C) Correlations between the Term Manifolds $\{\mu, \alpha, n\}$, $n > 1'$ *and* $\{\mu, \alpha, 1'\}$

Correlations between term values from the manifolds $\{\mu, \alpha, n\}$, $n > 1'$, and $\{\mu, \alpha, 1'\}$ offer several advantages. For example, a one-to-one correspondence between the dependent term values $\{\mu, \alpha, n\}$ and the independent term values $\{\mu, \alpha, 1'\}$ must exist. Furthermore, reliably assigned term values are most abundant for the lowest-energy terms $\{\mu, \alpha, 1'\}$ — which is an essential requirement for an independent variable. Finally, and perhaps most importantly, the correlations $\{\mu, \alpha, n\} \sim \{\mu, \alpha, 1'\}$ should exhibit a regular behavior of the coefficients of Eqs. (4.9, 11) with increasing n.

The matrix elements Q_{10}, Q_{11} of Eq. (4.3) and the matrix elements Q_{20}, Q_{21}, Q_{22} of Eq. (4.5) collect all relevant contributions from the first- and second-order perturbations in Equation (3.2). All these perturbations are electrostatic and are generated by charge distributions which possess zero monopoles; therefore, they are relatively short-ranged. Recalling our assumption (A1) concerning the small amplitude of Rydberg orbitals inside and near the core, we can expect, for a given μ and α, that the matrix elements Q_{ij} will decrease rapidly with increasing n. From the definitions of the coefficients K_{10} and K_{11} [Eq. (4.7)], and K_{20}, K_{21} and K_{22} [Eq. (D.3)], it follows that the coefficients $K_{ij}\begin{pmatrix}\mu\ \alpha\ n\\ \mu\ \alpha\ m\end{pmatrix}$, $n > m$, should also decrease with increasing n.

Granted this behavior of the coefficient

$$K_{ij}\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;m\end{pmatrix}, \qquad n > 1',$$

that part of the interatomic and intermolecular variability which is conditioned by Eqs. (4.6) and (4.8) is expected to decrease to zero with increasing n. In other words, for large enough n the one-electron component of the term values $\{\mu, \alpha, n\}$ will remain constant within the correlated atomic or molecular group and may be identified with the term value $T(\bar{\mathrm{X}}, \mu, \alpha, n)$ of the average chromophore $\bar{\mathrm{X}}$. At this point, it is appropriate to emphasize that the elimination of $(N_{\mathrm{X}} - \bar{N})$ from Eq. (4.4) in the manner which produced Eq. (4.8) was based on the assumption that

$$|Q_{2i}(\mu, \alpha, n)| < |Q_{2i}(\nu, \beta, m)|, \quad i = 0, 1, 2.$$

Thus, Eq. (4.8) is valid only for $n > m$.

Consider now Eq. (4.9) for the case of $(\nu, \beta, m) \equiv (\mu, \alpha, 1')$. As discussed, the slope $b_1\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$ is expected to approach zero with increasing n. The intercept $a_1\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$ can be separated into three components

$$\begin{aligned} a_1\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix} = & \left\{ T(\bar{\mathrm{X}}, \mu, \alpha, n) - T(\bar{\mathrm{X}}, \mu, \alpha, 1')\, b_1\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix}\right\} \\ & - (Z-1)\left\{ \langle \mu, \alpha, n \,|\, v_{01} \,|\, \mu, \alpha, n\rangle \right. \\ & \qquad \left. - \langle \mu, \alpha, 1' \,|\, v_{01} \,|\, \mu, \alpha, 1'\rangle\, b_1\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix}\right\} \\ & - \left\{ \langle \mu, \alpha, n \,|\, v_{\mathrm{S}} \,|\, \mu, \alpha, n\rangle \right. \\ & \qquad \left. - \langle \mu, \alpha, 1' \,|\, v_{\mathrm{S}} \,|\, \mu, \alpha, 1'\rangle\, b_1\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix}\right\}. \end{aligned} \tag{5.1}$$

The first component, which collects the zero-order contributions, is, according to definition, dependent only on the average chromophore $\bar{\mathrm{X}}$. Thus, this component should be transferable between atomic (or molecular) groups which have a common $\bar{\mathrm{X}}$. The second term reflects the dependence of the term values on the net core charge Z. For neutral species XS (for which $Z = 1$), this term vanishes. Since atoms are the only species with $Z \geqq 2$ for which term values are commonly available, the second term of Eq. (5.1) is of little practical importance for molecules. The third term of Eq. (5.1) gives the contribution from the substituent charge density $\varrho(\boldsymbol{r}; S/\bar{\mathrm{X}}, \mu)$ and for a given S, this term is dependent only on the average chromophore $\bar{\mathrm{X}}$ (see Appendices B, C). Thus, we may expect that correlations for molecular groups with different substituents S but a common average chromophore $\bar{\mathrm{X}}$ will produce a set of parallel linear dependencies for every fixed (μ, α, n).

The expressions for the coefficients $a_2\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$ and $b_2\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$, which are explicit in the individual perturbing potentials, are lengthy and are not presented here. For atomic systems, the coefficient a_2 contains contributions which are analogous to the first two terms of Eq. (5.1), and an additional second-order term which is quadratic (i.e., $(Z-1)^2$). Similarly, b_2 contains terms equivalent to b_1 and a second-order correction which is linear [i.e., $(Z-1)$]. In the case of molecules with $Z = 1$, a_2 contains zero-order terms which depend only on the average chromophore, and first- and second-order contributions which arise from the substituent potential. The coefficient b_2 becomes substituent dependent via second-order corrections.

We have not as yet considered any possible dependence of the term values of the average chromophore on the net core-charge Z. From studies of Rydberg term values within isoelectronic atomic series, it is known that, for given (μ, α, n), the term values within the series are proportional [1, 2] to Z^2. We will assume that the same dependence holds for the term values of $\bar{\mathrm{X}}_Z$, where $\bar{\mathrm{X}}_Z$ denotes the average chromophore with net charge Z. Thus we write

$$T(\bar{\mathrm{X}}_Z, \mu, \alpha, n) = Z^2\, T(\bar{\mathrm{X}}_1, \mu, \alpha, n) \tag{5.2}$$

Eq. (5.2), combined with the correlations of Eq. (4.9) for the case of atomic systems, and for $(\nu, \beta, m) \equiv (\mu, \alpha, 1')$, yields

$$\begin{aligned} \frac{T_1(\mathrm{X}_Z, \mu, \alpha, n)}{Z^2} = & \; d_1\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix} + \frac{Z-1}{Z^2}\, d_2\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix} \\ & + d_3\begin{pmatrix}\mu\,\alpha\,n\\ \mu\,\alpha\,1'\end{pmatrix} \frac{T_1(\mathrm{X}_Z, \mu, \alpha, 1')}{Z^2}, \end{aligned} \tag{5.3}$$

where $d_1\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$ is simply the first line of Eq. (5.1) divided by Z^2; $d_2\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$ is the parenthesized part of the second line of Eq. (5.1) divided by $-Z^2$ and $d_3\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$ is identical to $b_1\begin{pmatrix}\mu\;\alpha\;n\\ \mu\;\alpha\;1'\end{pmatrix}$. Under the same conditions, Eq. (4.11) yields

$$\frac{T_2(\mathrm{X}_Z,\mu,\alpha,n)}{Z^2} = f_1 + \frac{Z-1}{Z} f_2\left\{1+\frac{Z-1}{Z^2}F_2\right\} + f_3\left\{1+\frac{Z-1}{Z^2}F_3\right\}\frac{T_2(\mu,\alpha,1')}{Z^2} + f_4\frac{T_2(\mu,\alpha,1')^2}{Z^4}. \tag{5.4}$$

In Eq. (5.4), we have omitted the dependence of the parameters f_i and F_i on the indexes μ, α, n. The coefficients d_i of Eq. (5.3) and the coefficients f_i and F_i of Eq. (5.4) are dependent only on the monopositive average chromophore $\bar{\mathrm{X}}_1$. Therefore, within the validity of the approximations we have introduced, Eqs. (5.3, 4) offer correlative algorithms for relatively large atomic populations.

D) *Correlations between Rydberg Term Values and Ionization Potentials*

The ionization of a molecular or atomic species may involve the removal of an electron from a loosely bound orbital. (Examples are ionization from (i), a molecular "lone-pair" orbital; (ii), the highest energy ground-state π MO; and (iii), the outer-shell atomic orbitals.) With no pretense of rigor, we may suppose that nonbonding ground-state orbitals are similar to an excited state Rydberg orbital, and we may then presume to treat them on the same footing. Of course, in view of the impropriety of a one-electron model for core electrons, it is clear that any conclusions which may result from such a supposition will remain ambiguous until based on a more elaborate Hamiltonian [20]. We are justified in this extrapolation to core electrons only insofar as our purpose is to generate insights which may be of importance to a future treatment of Equation (1.1) [20].

With the above apology in mind, then, we shall suppose the ionization potentials $I(\mathrm{XS},\mu)$ of a nonbonding ground-state orbital to be one of the eigenvalues of Eq. (2.1) with eigenfunction $\varphi(\mathrm{XS},\mu)$. Consequently, for $I(\mathrm{XS},\mu)$, we can write equations analogous to Eqs. (4.2, 4). Elimination of $(N_{\mathrm{X}}-\bar{N})$ by means of the first-order approximation to Eq. (4.2), rephrased for $I(\mathrm{XS},\mu)$, yields a linear dependence of term values on ionization energies, while the second-order approximation to Eq. (4.4) yields a quadratic dependence. Thus for correlations between the term values from a manifold $\{\mu,\alpha,n\}$, $n \geqq 1'$, and the corresponding ionization limit $I(\mathrm{XS},\mu)$, we have

$$T_1(\mathrm{XS},\mu,\alpha,n) = a_1(\mu,\alpha,n) + b_1(\mu,\alpha,n)\,I_1(\mathrm{XS},\mu), \tag{5.5}$$

$$T_2(\mathrm{XS},\mu,\alpha,n) = a_2(\mu,\alpha,n) + b_2(\mu,\alpha,n)\,I_2(\mathrm{XS},\mu) + c_2(\mu,\alpha,n)\,I_2(\mathrm{XS},\mu)^2, \tag{5.6}$$

where $I_1(\mathrm{XS},\mu)$ and $I_2(\mathrm{XS},\mu)$ are the first-order and the second-order estimates of $I(\mathrm{XS},\mu)$ and a_1, b_1, a_2, b_2, c_2 are defined analogously to the coefficients of Eqs. (4.9, 11). Neglecting all second- and higher-order corrections, Eq. (5.5) is a mimic of Equation (1.1).

The dependence of the coefficients in Eqs. (5.5, 6) on the average chromophore $\bar{\mathrm{X}}$, the substituent S and the net core charge Z is identical to that of the previous Section. However, the amplitude of $\varphi(\boldsymbol{r};\mathrm{XS},\mu)$ in proximity to the core is much larger than those of "proper" Rydberg type orbitals $\varphi(\boldsymbol{r};\mathrm{XS},\mu,\alpha,n)$. Therefore, for correlations of term values with their ionization limits, we expect that the correspondants of the coefficients K_{ij} will not only approach zero with increasing n but that they will be small quantities (relative to the zero order terms) even for the value $n = 1'$. For the same reasons, we foresee that all second-order corrections might well be statistically insignificant [21].

E) *Summary*

The primary aim of this work has been to generate an initial understanding, in the guise of perturbation theory, of existent [1—4] empirical Rydberg termvalue correlations. This has resulted in a derivation of Eq. (1.2) and a subsequent generalization of this empirical relation — a generalization which is amenable to further theoretical processing at a computational level. In arriving at this result, however, we have justified a number of additional empirical observations.

We have provided a theoretical understanding of the utility [1—3] of a simple serial indexing, as opposed to an *aufbau* labelling, for Rydberg states.

We have achieved an inductive validation for the separation of a molecule into a Rydberg chromophoric part and a substituent part [1].

We have provided a theoretical interpretation of the concept of an "average chromophore" — a concept which has been shown [1, 2] to be important as a criterion for membership in an atomic or molecular class; and we have elucidated, qualitatively, the deviations of individual chromophores from this "average chromophore".

Appendix A

Consider a molecule or atom with $N+1$ electrons and, in correspondence with it, a cation with N electrons. We assume that the $(N+1)$-electron and N-electron systems have an identical nuclear distribution given by the vector set $\{\boldsymbol{R}_\omega\}$, where $\omega = 1, \ldots, K$ and where K is the number of nuclei. The electronic Hamiltonian of the $(N+1)$-electron species can be written as

$$\hat{H}(1, \ldots, N+1) = \hat{H}(1) + \hat{H}(2, \ldots, N+1) + \hat{G}(1; 2, \ldots, N+1) \quad \text{(A.1)}$$

In Eq. (A.1), the Hamiltonian $\hat{H}(1)$ describes a single electron in the electrostatic field of all K nuclei

$$\hat{H}(1) = -(\hbar^2/2m)\Delta(1) - e^2 \sum_{\omega=1}^{K} Z_\omega/|\boldsymbol{r}_1 - \boldsymbol{R}_\omega|, \quad \text{(A.2)}$$

where Z_ω is the atomic number of the ωth nucleus and $\boldsymbol{r}_1$ is the position vector of the electron considered. The Hamiltonian $\hat{H}(2, \ldots, N+1)$ is the electronic Hamiltonian of the N-electron cationic species and $\hat{G}(1; 2, \ldots, N+1)$, which represents the interactions between a single electron and the N-electron subsystem, is given by

$$\hat{G}(1; 2, \ldots, N+1) = \sum_{i=2}^{N+1} \hat{g}(1, i) \quad \text{(A.3)}$$

We now assume that those electronic wavefunctions of the $(N+1)$-electron species which correspond to Rydberg-type states may be approximated by an antisymmetrized product of a one-electron function $\varphi(1)$ and an (antisymmetrized) N-electron function $\Phi(2, \ldots, N+1)$

$$\psi(1, 2, \ldots, N+1) = \mathscr{A}\varphi(1)\Phi(2, \ldots, N+1) \quad \text{(A.4)}$$

We also impose the following orthogonality restriction on the functions φ and Φ [22]:

$$\int \mathrm{d}\tau_k \Phi(\ldots k \ldots)\varphi(k) = 0; \quad k = 2, \ldots, N+1, \quad \text{(A.5)}$$

where τ_k represents the space and spin variables for the kth electron. Finally, the antisymmetrizer $\mathscr{A}$ may be expressed in terms of the identity permutation $\hat{e}$ and the transpositions $\hat{t}_{1i}$

$$\mathscr{A} = [1/(N+1)]\left\{\hat{e} - \sum_{i=2}^{N+1} \hat{t}_{1i}\right\}. \quad \text{(A.6)}$$

The expectation value of the Hamiltonian of Eq. (A.1) and the norm of the function of Eq. (A.4) follow immediately from Eqs. (A.1—6) and are

$$\langle\psi|\hat{H}|\psi\rangle = [1/(N+1)]\langle\varphi(1)|\hat{H}(1) + \langle\Phi(2, \ldots, N+1)|\sum_{i=2}^{N+1}\hat{g}(1, i)[\hat{e} - \hat{t}_{1i}] + \hat{H}(2, \ldots, N+1)|\Phi(2, \ldots, N+1)\rangle|\varphi(1)\rangle, \quad \text{(A.7)}$$

$$\langle\psi|\hat{I}|\psi\rangle = [1/(N+1)]\langle\varphi(1)|\langle\Phi(2, \ldots, N+1)|\hat{I}|\Phi(2, \ldots, N+1)\rangle|\varphi(1)\rangle. \quad \text{(A.8)}$$

If we now choose the function Φ to be the μth eigenfunction Φ_μ of $\hat{H}(2, \ldots, N+1)$ and if we let E_μ denote the eigenvalue corresponding to Φ_μ, we find that the minimization of Eq. (A.7) (constrained by Eq. (A.8) with respect to φ yields the following eigenequation for φ

$$\left\{\hat{H}(1) + \langle\Phi_\mu(2, \ldots, N+1)| \cdot \sum_{i=2}^{N+1}\hat{g}(1, i)[\hat{e} - \hat{t}_{1i}]|\Phi_\mu(2, \ldots, N+1)\rangle - \varepsilon\hat{I}\right\}|\varphi(1)\rangle = 0. \quad \text{(A.9)}$$

The eigenvalue ε is related to E_μ and to the expectation value $\langle\Psi|\hat{H}|\psi\rangle \equiv E$ as $\varepsilon = E - E_\mu$. If, further, we denote the electronic ground state energy of the $(N+1)$-electron species by E_0, we can write $-\varepsilon = (E_\mu - E_0) - (E - E_0)$. Since the quantities $(E_\mu - E_0)$ and $(E - E_0)$ may be interpreted as the ionization and excitation energies, respectively, $-\varepsilon$ represents a term value of a Rydberg state and the function $\varphi(1)$ represents a Rydberg spin-orbital.

Introduction of the first-order density matrix [23] $\Gamma(2'|2)$

$$\Gamma_\mu(2'|2) = \int \mathrm{d}\tau_3 \ldots \int \mathrm{d}\tau_{N+1} \Phi_\mu^*(2', 3, \ldots, N+1) \Phi_\mu(2, 3, \ldots, N+1) \quad \text{(A.10)}$$

into Eq. (A.9) yields

$$\{\hat{H}(1) + N \int \mathrm{d}\tau_2 \hat{g}(1,2)[\hat{e} - \hat{t}_{12}] \Gamma_\mu(2'|2) - \varepsilon \hat{I}\} | \varphi(1) \rangle = 0 . \tag{A.11}$$

At this point, we assume that $\hat{g}(1, 2) = e^2/|\boldsymbol{r}_1 - \boldsymbol{r}_2|$ (i.e., we neglect all but electrostatic interactions between the electron in orbital $\varphi(1)$ and the N-electron subsystem) [10]. We also introduce an assumption which is considerably more stringent than that of Eq. (A.5): We set $\Phi(\ldots k \ldots)^* \varphi(k) = 0$. This zero differential-overlap approximation permits us to disregard the exchange terms of Equation (A.11). With these assumptions, Eq. (A.11) reduces to

$$\{\hat{H}(1) + e^2 N \int \mathrm{d}\boldsymbol{r}_2 |\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-1} \Gamma_\mu(\boldsymbol{r}_2) - \varepsilon \hat{I}\} | \varphi(1) \rangle = 0 , \tag{A.12}$$

where $\Gamma_\mu(\boldsymbol{r})$ is the spinless electron density.

Appendix B

Partitioning of Core Charge Density: The spinless electron density $\Gamma(\boldsymbol{r})$ associated with the N-electron function $\Phi(1, \ldots, N)$ can be obtained as the expectation value of the operator $\hat{\Gamma}$, where

$$\hat{\Gamma} \equiv (1/N) \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i); \tag{B.1}$$

and where $\delta(\boldsymbol{r} - \boldsymbol{r}_i)$ is the three-dimensional Dirac delta function. That is, we can write

$$\Gamma(\boldsymbol{r}) = \langle \Phi(1, \ldots, N) | \hat{\Gamma} | \Phi(1, \ldots, N) \tag{B.2}$$

Assume now that

$$\{\Phi_\alpha^{(\mathrm{a})}(1, \ldots, N_\mathrm{a})\} \quad \text{and} \quad \{\Phi_\alpha^{(\mathrm{b})}(1, \ldots, N_\mathrm{b})\}$$

are two orthonormal sets of antisymmetric functions such that a given normalized antisymmetric function $\Phi(1, \ldots, N)$, $N = N_\mathrm{a} + N_\mathrm{b}$, can be expanded over the product base $\Phi_\alpha^{(\mathrm{a})} \Phi_\beta^{(\mathrm{b})}$ as

$$\Phi(1, \ldots, N) = \mathscr{A}_{\mathrm{ab}} \sum_{\alpha, \beta} A_{\alpha\beta} \Phi_\alpha^{(\mathrm{a})}(1, \ldots, N_\mathrm{a}) \cdot \Phi_\beta^{(\mathrm{b})}(N_\mathrm{a} + 1, \ldots, N) \tag{B.3}$$

where $\mathscr{A}_{\mathrm{ab}}$ is an appropriate antisymmetrizer. Substitution of the expansion of Eq. (B.3) into Eq. (B.2) yields:

$$\Gamma(\boldsymbol{r}) = (N_\mathrm{a}/N) \Gamma(\boldsymbol{r}; \mathrm{a/b}) + (N_\mathrm{b}/N) \Gamma(\boldsymbol{r}; \mathrm{b/a}) \tag{B.4}$$

(The symbol a/b in $\Gamma(\boldsymbol{r}; \mathrm{a/b})$ is used in order to emphasize the dependence of the a-component of Γ on the nature of b; an analogous role is played by the symbol b/a in $\Gamma(\boldsymbol{r}; \mathrm{b/a})$.) The components $\Gamma(\boldsymbol{r}; \mathrm{a/b})$ and $\Gamma(\boldsymbol{r}; \mathrm{b/a})$ of the density $\Gamma(\boldsymbol{r})$ are given by

$$\Gamma(\boldsymbol{r}; \mathrm{a/b}) = \sum_{\alpha, \alpha'} \sum_{\beta} A_{\alpha\beta}^* A_{\alpha'\beta} \langle \Phi_\alpha^{(\mathrm{a})}(1, \ldots, N_\mathrm{a}) \cdot | \hat{\Gamma}_\mathrm{a} | \Phi_{\alpha'}^{(\mathrm{a})}(1, \ldots, N_\mathrm{a}) \rangle , \tag{B.5}$$

$$\Gamma(\boldsymbol{r}; \mathrm{b/a}) = \sum_{\alpha, \alpha'} \sum_{\beta} A_{\beta\alpha}^* A_{\beta\alpha'} \langle \Phi_\alpha^{(\mathrm{b})}(1, \ldots, N_\mathrm{b}) \cdot | \hat{\Gamma}_\mathrm{b} | \Phi_{\alpha'}^{(\mathrm{b})}(1, \ldots, N_\mathrm{b}) \rangle , \tag{B.5}$$

where

$$\hat{\Gamma}_\mathrm{c} \equiv (1/N_\mathrm{c}) \sum_{i=1}^{N_\mathrm{c}} \delta(\boldsymbol{r} - \boldsymbol{r}_i); \; \mathrm{c} \in \{\mathrm{a}, \mathrm{b}\} . \tag{B.6}$$

Notice that, because of the orthonormality of the functions $\Phi^{(\mathrm{a})}$ and $\Phi^{(\mathrm{b})}$, the densities $\Gamma(\boldsymbol{r})$, $\Gamma(\boldsymbol{r}; \mathrm{a/b})$ and $\Gamma(\boldsymbol{r}; \mathrm{b/a})$ are normalized to unity. Combined with some tedious arithmetic, the expansion of Eq. (B.3) results in a partitioning of the first-order density matrix $\Gamma(1'|1)$ in a form analogous to that of Eq. (B.4), namely

$$\Gamma(l'|l) = (N_\mathrm{a}/N) \Gamma(1'|1; \mathrm{a/b}) + (N_\mathrm{b}/N) \Gamma(1'|1; \mathrm{b/a}) . \tag{B.7}$$

Partitioning of Core Electrostatic Potential: Since the Hamiltonian $\hat{H}(\boldsymbol{r}; \mathrm{XS}, \mu)$ of Eq. (2.1) takes account only of the Coulomb interactions between the rigid core XS⁺ and the optical electron, it follows that the potential energy part of $\hat{H}$ is represented by

$$V(\boldsymbol{r}; \mathrm{XS}, \mu) = e^2 \int \mathrm{d}\boldsymbol{r}' \varrho(\boldsymbol{r}'; \mathrm{XS}, \mu) |\boldsymbol{r}' - \boldsymbol{r}|^{-1} , \tag{B.8}$$

where $\varrho(\boldsymbol{r}; \mathrm{XS}, \mu)$ is the charge density (in $|e|$ units) of the XS⁺ core. From assumption A1, the density is identical to that of the μth state of the cation XS⁺.

We may take explicit account of the electronic and nuclear contributions to the density ϱ by writing [24]

$$\varrho(\boldsymbol{r}; \mathrm{XS}, \mu) = N \Gamma(\boldsymbol{r}; \mathrm{XS}, \mu) - \sum_{\omega=1}^{K} Z_\omega \delta(\boldsymbol{r} - \boldsymbol{R}_\omega) . \tag{B.9}$$

From the unit normalization of $\Gamma(\boldsymbol{r}; \mathrm{XS}, \mu)$ discussed above, we find

$$\int \mathrm{d}\boldsymbol{r} \, \varrho(\boldsymbol{r}; \mathrm{XS}, \mu) = N - \sum_{\omega=1}^{K} Z_\omega \equiv -Z , \tag{B.10}$$

where Z is the total charge (in $|e|$ units) of the XS⁺ core.

Substitution of Eq. (B.4) (with a = X, b = S) into Eq. (B.9) yields

$$\varrho(\boldsymbol{r}; \mathrm{XS}, \mu) = \varrho(\boldsymbol{r}; \mathrm{X/S}, \mu) + \varrho(\boldsymbol{r}; \mathrm{S/X}, \mu), \tag{B.11}$$

where

$$\varrho(\boldsymbol{r}; \mathrm{X/S}, \mu) = N_\mathrm{X} \Gamma(\boldsymbol{r}; \mathrm{X/S}, \mu) - \sum_\omega{}_\mathrm{X} Z_\omega \delta(\boldsymbol{r} - \boldsymbol{R}_\omega), \tag{B.12}$$

$$\varrho(\boldsymbol{r}; \mathrm{S/X}, \mu) = N_\mathrm{S} \Gamma(\boldsymbol{r}; \mathrm{S/X}, \mu) - \sum_\omega{}_\mathrm{S} Z_\omega \delta(\boldsymbol{r} - \boldsymbol{R}_\omega). \tag{B.13}$$

The summations $\sum_\omega{}_\mathrm{X}$ and $\sum_\omega{}_\mathrm{S}$ extend only over the chromophoric and substituent nuclei, respectively. In general, the nuclear positions $\boldsymbol{R}_\omega$ within the chromophore X are dependent upon the nature of S, and *vice versa*. However, we neglect all such polarizations of the nuclear distributions.

Given a partitioning of the core nuclei into chromophoric and substituent parts Eqs. (B.9—13) do not determine the electron partitioning $N = N_\mathrm{X} + N_\mathrm{S}$ uniquely. The ambiguity is removed by the implicit requirement of the assumption (A2) that the positive hole with monopole Z be entirely located on the chromophoric part of the XS⁺ core. Thus,

$$\int \mathrm{d}\boldsymbol{r}\, \varrho(\boldsymbol{r}; \mathrm{X/S}, \mu) = N_\mathrm{X} - \sum_\omega{}_\mathrm{X} Z_\omega = -Z, \tag{B.14}$$

$$\int \mathrm{d}\boldsymbol{r}\, \varrho(\boldsymbol{r}; \mathrm{S/X}, \mu) = N_\mathrm{S} - \sum_\omega{}_\mathrm{S} Z_\omega = 0. \tag{B.15}$$

Finally, substitution of Eqs. (B.12, 13) into Eq. (B.8) yields the partitioning of the core electrostatic potential into the components $V(\boldsymbol{r}; \mathrm{X/S}, \mu)$ and $V(\boldsymbol{r}; \mathrm{S/X}, \mu)$; application of Eqs. (B.14, 15) then leads to the asymptotic conditions of Eq. (2.2).

Appendix C

Expansion of Core Densities: Taking into account the restriction of Eq. (B.12), we can rewrite Eq. (B.14) as

$$\varrho(\boldsymbol{r}; \mathrm{X/S}, \mu) = -Z\delta(\boldsymbol{r}) + N_\mathrm{X}\{\Gamma(\boldsymbol{r}; \mathrm{X/S}, \mu) - \delta(\boldsymbol{r})\} - \sum_\omega{}_\mathrm{X} Z_\omega \{\delta(\boldsymbol{r} - \boldsymbol{R}_\omega) - \delta(\boldsymbol{r})\}. \tag{C.1}$$

The first term of Eq. (C.1) represents the monopole of the chromophoric charge density, and it is centered at a coordinate origin which is located inside the chromophore. The second and third terms of Eq. (C.1) are the electronic and nuclear charge distributions with zero monopoles. For monatomic chromophores (and, particularly, for atoms) for which the nucleus is located on the origin of coordinates, the third term of Eq. (C.1) vanishes.

We now write the electron density $\Gamma(\boldsymbol{r}; \mathrm{X/S}, \mu)$ as the sum of two terms

$$\Gamma(\boldsymbol{r}; \mathrm{X/S}, \mu) = \Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; \bar{\mathrm{X}}, \mu) + \Delta\Gamma(\boldsymbol{r}; \mathrm{X/S}, \mu),$$

where $\Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; \bar{\mathrm{X}}, \mu)$ is assumed to be normalized to one and to be a differentiable function of N_X and Z within a group of species with common $\bar{\mathrm{X}}$ and S. The quantity $\Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; \bar{\mathrm{X}}, \mu)$ is interpreted as that part of the chromophoric electron density which is independent of the substituent and which is smoothly variable within the group of the species XS. The term $\Delta\Gamma(\boldsymbol{r}; \mathrm{X/S}, \mu)$ represents that part of the chromophoric electron density which inhibits the treatment of the chromophore and substituent as truly independent entities. It is assumed (A2) that the contributions of $\Delta\Gamma$ to $V(\boldsymbol{r}; \mathrm{X/S}, \mu)$ are of second- and higher-orders only. The density $\Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; \bar{\mathrm{X}}, \mu)$ is now expanded in a power series about the average value of N_X, denoted $\bar{N}$, and about $Z = 1$

$$\Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; X, \mu) = \sum_{i=0} \sum_{j=0} (N_\mathrm{X} - \bar{N})^i (Z - 1)^j \Gamma_{ij}(\boldsymbol{r}), \tag{C.3}$$

where

$$\Gamma_{ij}(\boldsymbol{r}) = (i!\,j!)^{-1} \left(\frac{\partial}{\partial N_\mathrm{X}}\right)^i \left(\frac{\partial}{\partial Z}\right)^j \cdot \Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; \bar{\mathrm{X}}, \mu)\Big|_{Z=1}^{N_\mathrm{X}=\bar{N}}. \tag{C.4}$$

From the definition of Eq. (C.4) and the normalization condition imposed on $\Gamma(\boldsymbol{r}, N_\mathrm{X}, Z; \bar{\mathrm{X}}, \mu)$, it follows that

$$\int \mathrm{d}\boldsymbol{r}\, \Gamma_{ij}(\boldsymbol{r}) = \delta_{0i}\delta_{0j}. \tag{C.5}$$

Substitution of Eqs. (C.2) and (C.3) into Eq. (C.1) yields

$$\begin{aligned}\varrho(\boldsymbol{r}; \mathrm{X/S}, \mu) = {} & -Z\delta(\boldsymbol{r}) + \bar{N}\{\Gamma_{00}(\boldsymbol{r}) - \delta(\boldsymbol{r})\} \\ & + (N_\mathrm{X} - \bar{N})\{\bar{N}\Gamma_{10}(\boldsymbol{r}) + \Gamma_{00}(\boldsymbol{r}) - \delta(\boldsymbol{r})\} \\ & + (Z - 1)\bar{N}\Gamma_{01}(\boldsymbol{r}) + (N_\mathrm{X} - \bar{N})^2\{\bar{N}\Gamma_{20}(\boldsymbol{r}) \\ & + \Gamma_{10}(\boldsymbol{r})\} + (N_\mathrm{X} - \bar{N})(Z - 1)\{\bar{N}\Gamma_{11}(\boldsymbol{r}) \\ & + \Gamma_{01}(\boldsymbol{r})\} + (Z - 1)^2\bar{N}\Gamma_{02}(\boldsymbol{r}) + \cdots.\end{aligned} \tag{C.6}$$

In Eq. (C.6), all terms, excluding the first, represent a charge distribution with zero monopole; cubic and higher terms of Eq. (C.4), as well as contributions from $\Delta\Gamma(\boldsymbol{r};\ \mathrm{X/S},\ \mu)$, are not included in the expansion of Eq. (C.6).

The substituent charge density $\varrho(\boldsymbol{r};\ \mathrm{S/X},\ \mu)$ can be written in a form analogous to Eq. (C.2) as

$$\begin{aligned}
&\varrho(\boldsymbol{r};\ \mathrm{S/X},\ \mu)\\
&= N_{\mathrm{S}}\{\Gamma(\boldsymbol{r};\ \mathrm{S/\bar{X}},\ \mu) - \sum_{\omega}{}_{\mathrm{S}} Z_{\omega}\,\delta(\boldsymbol{r} - \boldsymbol{R}_{\omega})\}\\
&\quad + N_{\mathrm{S}}\Delta\Gamma(\boldsymbol{r};\ \mathrm{S/X},\ \mu), \qquad \text{(C.7)}
\end{aligned}$$

where $\Gamma(\boldsymbol{r};\ \mathrm{S/X},\ \mu)$ is normalized to unity and represents the substituent part of the electron density of the species $\bar{\mathrm{X}}\mathrm{S}^{+}$. The term $\Delta\Gamma(\boldsymbol{r};\ \mathrm{S/X},\ \mu)$ is interpreted in a manner similar to that of $\Delta\Gamma(\boldsymbol{r};\mathrm{X/S},\ \mu)$; its contribution to the core potential is assumed (A2) to be negligible, at least to first-order accuracy.

Expansion of Core Hamiltonian: The expansions given in Eqs. (C.6, 7), when conbined with Eqs. (2.3) and (B.8), yield the Hamiltonian $\hat{H}(\boldsymbol{r};\ \mathrm{XS},\ \mu)$ of Equation (3.2). The potentials v_{10}, v_{01}, v_{S}, v_{20}, v_{11} and v_{02} are defined as follows:

$$\begin{aligned}
v_{01}(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{r}'\,|\boldsymbol{r} - \boldsymbol{r}'|^{-1}\\
&\quad\cdot \{\bar{N}\Gamma_{10}(\boldsymbol{r}') + \Gamma_{00}(\boldsymbol{r}') - \delta(\boldsymbol{r})\},\\
v_{10}(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{r}'\,|\boldsymbol{r} - \boldsymbol{r}'|^{-1}\bar{N}\Gamma_{01}(\boldsymbol{r}'),\\
v_{\mathrm{S}}(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{r}'\,|\boldsymbol{r} - \boldsymbol{r}'|^{-1}N_{\mathrm{S}}\\
&\quad\cdot \{\Gamma(\boldsymbol{r}';\ \mathrm{S/X},\ \mu) - \sum_{\omega}{}_{\mathrm{S}}\,\delta(\boldsymbol{r}' - \boldsymbol{R}_{\omega})\},\\
v_{20}(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{r}'\,|\boldsymbol{r} - \boldsymbol{r}'|^{-1}\\
&\quad\cdot \{\bar{N}\Gamma_{20}(\boldsymbol{r}') + \Gamma_{10}(\boldsymbol{r}')\},\\
v_{11}(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{r}'\,|\boldsymbol{r} - \boldsymbol{r}'|^{-1}\\
&\quad\cdot \{\bar{N}\Gamma_{11}(\boldsymbol{r}') + \Gamma_{01}(\boldsymbol{r}')\},\\
v_{02}(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{r}'\,|\boldsymbol{r} - \boldsymbol{r}'|^{-1}\bar{N}\Gamma_{02}(\boldsymbol{r}'). \qquad \text{(C.8)}
\end{aligned}$$

Appendix D

Equation (4.4) leads to a quadratic equation for variable $(N_{\mathrm{X}} - \bar{N})$. Abbreviating $N_{\mathrm{X}} - \bar{N}$ by ΔN, $T_2(\mu, \alpha, n) - T_0(\mu, \alpha, n)$ by ΔT_2, and the coefficients of Eq. (4.5) by Q_{20}, Q_{21} and Q_{22}, we find

$$\begin{aligned}
&\Delta N_{\pm} \qquad \text{(D.1)}\\
&= \left\{-1 \pm \left[1 + 4\,\frac{Q_{22}}{Q_{21}}\left(\frac{\Delta T_2 - Q_{20}}{Q_{21}}\right)\right]^{1/2}\right\} \Big/ \left(\frac{Q_{22}}{Q_{21}}\right).
\end{aligned}$$

Since Q_{22} contains contributions only from second-order perturbations and Q_{21} contains contributions from both first- and second-order perturbations [see Eqs. (4.5)], we choose that root of Eq. (D.1) which, for $Q_{22}/Q_{21} \ll 1$, approaches the ΔN evaluated from the first-order relation of Equation (4.2). The root ΔN_{+} possesses the correct behavior. Expansion of the square-root part of Eq. (D.1) as a power series around unity yields

$$\begin{aligned}
\Delta N_{+} = \frac{\Delta T_2 - Q_{20}}{Q_{21}}&\left[1 - \frac{Q_{22}}{Q_{21}}\left(\frac{\Delta T_2 - Q_{20}}{Q_{21}}\right)\right.\\
&\left. + 2\left(\frac{Q_{22}}{Q_{21}}\right)^2\left(\frac{\Delta T_2 - Q_{20}}{Q_{21}}\right)^2 + \cdots\right]. \qquad \text{(D.2)}
\end{aligned}$$

The elimination of ΔN_{+} from any pair of equations of the type of Eq. (4.4) and the subsequent neglect of all terms which are not linear in the second-order contributions or which are neither linear nor quadratic in the first-order contributions, gives the following expressions for the coefficients K_{22}, K_{21} and K_{20}:

$$\begin{aligned}
K_{22}\begin{pmatrix}\mu\ \alpha\ n\\ \nu\ \beta\ m\end{pmatrix} &= \frac{1}{Q_{21}(\nu, \beta, m)^2}\\
&\quad\cdot\left[Q_{22}(\mu, \alpha, n) - Q_{22}(\nu, \beta, m)\,\frac{Q_{21}(\mu, \alpha, n)}{Q_{21}(\nu, \beta, m)}\right],\\
K_{21}\begin{pmatrix}\mu\ \alpha\ n\\ \nu\ \beta\ m\end{pmatrix} &= \frac{Q_{21}(\mu, \alpha, n)}{Q_{21}(\nu, \beta, m)}\\
&\quad - 2\,Q_{20}(\nu, \beta, m)\,K_{22}\begin{pmatrix}\mu\ \alpha\ n\\ \nu\ \beta\ m\end{pmatrix},\\
K_{20}\begin{pmatrix}\mu\ \alpha\ n\\ \nu\ \beta\ m\end{pmatrix} &= Q_{20}(\mu, \alpha, n) - Q_{20}(\nu, \beta, m)\,K_{21}\begin{pmatrix}\mu\ \alpha\ n\\ \nu\ \beta\ m\end{pmatrix}\\
&\quad - Q_{20}(\nu, \beta, m)^2\,K_{22}\begin{pmatrix}\mu\ \alpha\ n\\ \nu\ \beta\ m\end{pmatrix}. \qquad \text{(D.3)}
\end{aligned}$$

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[10] Exchange and spin-orbit interactions, of course, are important and their neglect is justified only to the extent that this work be viewed as a first-order effort. This approximation will be removed in a later publication (P. Hochmann, G. L. Findley, and S. P. McGlynn, in preparation).

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