PHYSICAL REVIEW A VOLUME 37, NUMBER 4 FEBRUARY 15, 1988

van der Waals forces, sum rules, and pseudostate expansions

C. K. Au
Department of Physics and Astronomy, University of South Carolina, Columbia, South Carolina 29208

Richard J. Drachman
Laboratory for Astronomy and Solar Physics, Goddard Space Flight Center, Greenbelt, Maryland 20771

(Received 20 April 1987)

We reexamine the pseudostate expansion used previously to evaluate van der Waals (vdW) coefficients and finite-mass corrections. In particular, we wish to understand the very rapid convergence of the expansion, which for the case of two hydrogenic atoms requires only ten terms to achieve an accuracy of 1×10^{-10}. The analysis proceeds from the representation of the vdW coefficients as integrals of single-atom frequency-dependent polarizabilities. These in turn can be expanded in power series with coefficients of the form $\sum_n M^2(nl)/(E_{nl}-E_{1s})^k$, where $M(nl)$ is a multipole matrix element between the ground (1s) and excited (nl) states. Although defined as sums over an infinite set of hydrogenic states, the coefficients of each order k are reproduced exactly by a finite sum over suitable pseudostates. By analytic continuation, the frequency-dependent polarizabilities computed using pseudostates are expected to be very close to the exact values, and hence the rapid convergence of the vdW coefficients is understood.

I. INTRODUCTION

We will be concerned in this paper with the computation of long-range (but unretarded) interactions between hydrogenic systems in their nondegenerate ground states. The well-known van der Waals potential is the leading term in an asymptotic series in inverse powers of the interatomic distance R and has the form $-C_6/R^6$; it results from the interaction of dipole moments induced in each of the atoms. Further terms result from higher multipole moments, each successively higher moment corresponding to a more rapid decrease of the potential by two additional powers of R; for example, the dipole-quadrupole interaction has the form $-C_8/R^8$. The literature[1] is full of thorough discussions of these adiabatic or Born-Oppenheimer potentials which are derived by holding the individual atoms fixed and solving (in some approximation) for the quantum-mechanical motion of the electrons. More recently, in connection with the interaction of positronium atoms (Ps), it has become of interest to investigate certain mass-dependent corrections to the usual adiabatic potentials.[2,3]

One of the most effective methods to compute the actual values of these coefficients makes use of the so-called pseudostate expansion.[4,5] When used in a variational derivation of C_6 the result is a formal expression that resembles conventional second-order perturbation theory with the usual infinite sum over intermediate states replaced by a finite sum over certain orthonormal functions. The remarkable fact is that only a few terms in this sum are needed to achieve very high accuracy in the evaluation of the coefficient. In an earlier work[3] we also used the pseudostate expansion to compute some of the mass-dependent correction coefficients with equal success. It is the purpose of this paper to examine and understand this rapid convergence.

The plan of the analysis is the following. We will first write the van der Waals (vdW) coefficients and their corrections as a conventional double summation over single-atom matrix elements. These will be rewritten in the form of an integral over the single-atom dynamic polarizabilities, which can each be expanded in a power series in the frequency. Finally, each of the coefficients of these series is seen to be related to a particular multipole sum rule, whose exact value can be given for the hydrogenic cases of interest here. It will then be proven that a finite pseudostate expansion is capable of exactly representing a finite subset of these sum rules and, hence, approximating the coefficients of the power series. Hence the analytic continuation of the power series is expected to give very accurate values of the van der Waals coefficients. Numerical results are given where they are appropriate to illustrate the mathematical points being made.

II. THE BASIC PROBLEM

The fundamental quantities needed for the calculation of vdW coefficients and their generalizations are double summations over excited intermediate states of the two interacting systems. (For simplicity we will assume identical hydrogen atoms, although other one-electron ions and positronium atoms can be easily treated.) These are[1,3]

$$Q_k(ll')=\sum_{nn'}\frac{M^2(nl)M^2(n'l')}{[\Delta(nl)+\Delta(n'l')]^k}\ , \qquad (1)$$

where $M(nl)=\langle nl\mid 2r^lP_l\mid 1s\rangle$ and $\Delta(nl)=E_{nl}-E_{1s}$ for multipole order l. These double sums cannot be carried out exactly. The usual van der Waals expansion is

$$V=-\sum_{n=3}\frac{C_{2n}}{R^{2n}} \text{ where } C_6=\tfrac{3}{2}Q_1(11),\quad C_8=\tfrac{15}{2}Q_1(12),\quad \text{and } C_{10}=14Q_1(13)+\tfrac{35}{2}Q_1(22)\ . \tag{2}$$

Certain mass-dependent nonadiabatic terms were defined in Ref. 3 and their coefficients have the following forms:

$$D=\tfrac{3}{2}Q_2(11) \text{ and } G=\tfrac{3}{2}Q_3(11)\ . \tag{3}$$

To begin the analysis we rewrite Q_k as a parametric integral,

$$Q_k(ll')=\frac{2}{\pi}\text{Re}\int_0^\infty d\omega\,\alpha_l(\omega)\beta_{l'k}(\omega)\ , \tag{4}$$

where α and β, related to the dynamic polarizabilities,[6] are defined as follows:

$$\alpha_l(\omega)=\sum_n\frac{M^2(nl)\Delta(nl)}{\Delta^2(nl)+\omega^2},\quad \beta_{lk}(\omega)=\sum_n\frac{M^2(nl)}{[\Delta(nl)+i\omega]^k}\ . \tag{5}$$

These can be expanded for small values of ω,

$$\begin{aligned}\alpha_l(\omega)&=\sum_{j=0}^{\infty}(-\omega^2)^jS_{l,2j+1}\ ,\\ \text{Re}\beta_{lk}(\omega)&=\sum_{j=0}^{\infty}(-\omega^2)^j\frac{(2j+k-1)!}{(2j)!(k-1)!}S_{l,2j+k}\ ,\end{aligned} \tag{6}$$

where $S_{l,m}=\sum_n M^2(nl)/[\Delta(nl)]^m$. We have thus succeeded in writing the original expression for $Q_k(ll')$ in terms of two power series in ω^2 whose coefficients are the negative-power energy-weighted sums $S_{l,m}$ each of which can be evaluated analytically.[7] We understand the dynamic polarizabilities (which can themselves be calculated analytically[6]) to be the analytic continuations of these power series beyond their rather limited circles of convergence.

The pseudostate method begins with a choice of N_0 basis functions of angular momentum l taken to have the form

$$\phi_{lj}(r)=e^{-r}r^{l+j}P_l\quad (j=0,1,\ldots,N_0-1)\ , \tag{7}$$

and linear combinations of these are next used to diagonalize approximately the hydrogen Hamiltonian ($H_0=-\nabla^2-2/r$ in Rydberg units)

$$\begin{aligned}\psi_{Nl}&=\sum_j C_l(N,j)\phi_{lj}\ ,\\ \langle Nl\,|\,H_0\,|\,N'l\rangle&=\bar{E}_{Nl}\delta_{NN'} \text{ and } \langle Nl\,|\,N'l\rangle=\delta_{NN'}\ .\end{aligned} \tag{8}$$

In this method $Q_k(ll')$ is approximated by simply replacing the infinite sum over the complete set of hydrogen states $|\,nl\,\rangle$ by a finite sum over the discrete set of pseudostates $|\,Nl\,\rangle$, with the energies E_{nl} replaced by the corresponding pseudoenergies $\bar{E}_{Nl}$. In practice, a ten-term expansion of this type gives ten-figure accuracy in the vdW coefficient.[4,5] To understand this rapid convergence we will return for a closer look at the properties of the dynamic polarizabilities and their power-series expansions.

Clearly, the pseudostate approximation to Q_k (denoted by a bar, as are all such approximate expressions from now on) can be written in terms of approximate dynamic polarizabilities as in Eq. (4). These, in turn, can be expanded in a power series in ω^2 [as in Eqs. (6)] whose coefficients are the approximate weighted sums $\bar{S}_{l,m}$. These are defined as follows:

$$\bar{S}_{l,m}=\sum_{N=1}^{N_0}\frac{\bar{M}^2(Nl)}{[\bar{\Delta}(Nl)]^m} \text{ where } \bar{M}(Nl)=\langle Nl\,|\,2r^lP_l\,|\,1s\,\rangle \text{ and } \bar{\Delta}(Nl)=\bar{E}_{Nl}-E_{1s}\ . \tag{9}$$

If these approximate sums are accurate, then the dynamic polarizabilities will be accurate and the van der Waals coefficients will also be good.

III. PROOF OF THE THEOREM

To establish the accuracy of the approximate sums we will now prove[8] that $\bar{S}_{l,m}=S_{l,m}$ for $m\leq 2(N_0-1)$.

First, let us show that $\bar{S}_{l,1}$ can be obtained by a variational calculation. We introduce a perturbed Hamiltonian H and construct a trial function from the pseudostates,

$$|\,\Psi_l\,\rangle=|\,1s\,\rangle+\sum_{N=1}^{N_0}C_{Nl}\,|\,Nl\,\rangle \text{ and } H=H_0+\lambda V_l\ , \tag{10}$$

where $V_l=2r^lP_l$, and, hence, $\langle\,1s\,|\,Nl\,\rangle=0$. To first order in the small parameter λ, the Rayleigh-Ritz variational principle gives the following expression for the expansion coefficients:

$$C_{Nl}=-\frac{\lambda\langle\,Nl\,|\,V_l\,|\,1s\,\rangle}{\bar{\Delta}(Nl)}$$

and

$$|\,\bar{\Psi}_l\,\rangle=|\,1s\,\rangle-\lambda\sum_{N=1}^{N_0}\frac{|\,Nl\,\rangle\langle\,Nl\,|\,V_l\,|\,1s\,\rangle}{\bar{\Delta}(Nl)}\ . \tag{11}$$

This evidently has exactly the form of the usual perturbation expression, although it involves only a finite sum on a set of normalizable functions. It is well known,[9,10] however, that the exact expression for the first-order perturbed wave function of the polarization perturbation has the form

$$|\,\Psi_l\,\rangle=|\,1s\,\rangle-\lambda\left[\frac{r^l}{l}+\frac{r^{l+1}}{l+1}\right]P_l\,|\,1s\,\rangle\ , \tag{12}$$

and this expression can be achieved with a two-term expansion of the type shown in Eq. (7). (We shall use wave-function and ket-vector notation interchangeably.) The variational method guarantees that we will obtain the exact energy and wave function *if* we provide a trial function of sufficiently general form. But the perturbed energy in this case is just

$$\Delta E = -\lambda^2 \sum_{N=1}^{N_0} \frac{\langle 1s \mid V_l \mid Nl \rangle \langle Nl \mid V_l \mid 1s \rangle}{\bar{\Delta}(Nl)} \equiv -\lambda^2 \bar{S}_{l,1} \tag{13}$$

and the wave-function normalization is

$$\langle \bar{\Psi}_l \mid \bar{\Psi}_l \rangle = 1 + \lambda^2 \sum_{N=1}^{N_0} \frac{\langle 1s \mid V_l \mid Nl \rangle \langle Nl \mid V_l \mid 1s \rangle}{[\bar{\Delta}(Nl)]^2}$$

$$\equiv 1 + \lambda^2 \bar{S}_{l,2} \; . \tag{14}$$

Thus we have proven that a two-term basis set ($N_0 = 2$) will give the sums $S_{l,1}$ and $S_{l,2}$ exactly; the former from the energy and the latter from the wave-function normalization.

To illustrate this point, we show the orthogonal basis functions in the two-state dipole ($l = 1$) approximation, their energies in Rydbergs, and show how the exact sum rule results from what has been discussed above,[5]

$$\begin{aligned}
&\mid 11 \rangle = \left[\frac{2}{15\pi} \right]^{1/2} r^2 e^{-r} P_1, \quad \bar{E}_{11} = -\tfrac{1}{5} \; , \\
&\bar{M}(11) = (\tfrac{10}{3})^{1/2}, \quad \bar{\Delta}(11) = \tfrac{4}{5} \; , \\
&\mid 21 \rangle = \left[\frac{2}{3\pi} \right]^{1/2} (3r - r^2) e^{-r} P_1, \quad \bar{E}_{21} = 1 \; , \\
&\bar{M}(21) = (\tfrac{2}{3})^{1/2}, \quad \bar{\Delta}(21) = 2 \; .
\end{aligned} \tag{15}$$

Using Eq. (15) in Eq. (11) we show easily that

$$\mid \bar{\Psi}_1 \rangle = -\frac{\bar{M}(11) \mid 1 \rangle}{\bar{\Delta}(11)} - \frac{\bar{M}(21) \mid 2 \rangle}{\bar{\Delta}(21)}$$

$$= -\frac{e^{-r}}{\sqrt{\pi}} \left[r + \frac{r^2}{2} \right] P_1 \; , \tag{16}$$

in agreement with the general expression in Eq. (12). By direct substitution it is also easy to show that $\bar{S}_{1,1} = \frac{9}{2}$ and $\bar{S}_{1,2} = \frac{43}{8}$, the well-known values of these sums. (In fact, the sums $\bar{S}_{1,0}$ and $\bar{S}_{1,-1}$ are also given exactly, a fact briefly discussed in the Appendix.) As expected, however, $\bar{S}_{1,3} = \frac{211}{32}$ is not correct in this approximation; however, it differs from the exact value $S_{1,3} = \frac{319}{48}$ by only about 1%.

To evaluate sum rules for $m > 2$ we use a simple trick to convert the expression into the form of a second-order perturbation sum, after which the variational method can be applied as above. If we define G_{lk} by

$$G_{lk} \mid 1s \rangle = (H_0 - E_{1s})^{-k} V_l \mid 1s \rangle \quad \text{where } G_{l0} = V_l \tag{17}$$

then $S_{l,2k+1}$ takes the form of a second-order energy shift with G_{lk} playing the role of the perturbing potential,

$$S_{l,2k+1} \equiv \sum_n \frac{\langle 1s \mid V_l \mid nl \rangle \langle nl \mid V_l \mid 1s \rangle}{[\Delta(nl)]^{2k+1}}$$

$$= -\sum \frac{\langle 1s \mid G_{lk} \mid nl \rangle \langle nl \mid G_{lk} \mid 1s \rangle}{\Delta(nl)} \; . \tag{18}$$

This is just the second-order energy shift when G_{lk} is considered to be the perturbation. Just as in the $k=0$ case, a variational trial function [Eq. (10)] will have the form of Eq. (11), with V_l replaced by G_{lk}. That is,

$$\bar{S}_{l,2k+1} = \sum_{N=1}^{N_0} \frac{\langle 1s \mid G_{lk} \mid Nl \rangle \langle Nl \mid G_{lk} \mid 1s \rangle}{\bar{\Delta}(Nl)} \; . \tag{19}$$

From Eq. (17) we can write

$$G_{lk} \mid 1s \rangle = \sum_{N=1}^{N_0} \frac{\mid Nl \rangle \langle Nl \mid V_l \mid 1s \rangle}{[\bar{\Delta}(Nl)]^k} \tag{20}$$

provided that $G_{lk} \mid 1s \rangle$ can be represented by a finite ($N \le N_0$) expansion in $\mid Nl \rangle$. Then substituting Eq. (20) into Eq. (19) we can write

$$\bar{S}_{l,2k+1} = \sum_{N=1}^{N_0} \frac{\langle 1s \mid V_l \mid Nl \rangle \langle Nl \mid V_l \mid 1s \rangle}{[\bar{\Delta}(Nl)]^{2k+1}} \; , \tag{21}$$

with a similar expression holding for $\bar{S}_{l,2k+2}$. Again, if the trial function is sufficiently general, Eq. (20) is valid, and the variational principle will guarantee that $\bar{S}_{l,2k+1} = S_{l,2k+1}$ (from the "energy" minimization) and $\bar{S}_{l,2k+2} = S_{l,2k+2}$ (from the normalization).

To complete the proof, we simply note[7,11] that each successive G contains one additional power of r. We prove this by induction. Let us write $G_{lk} = g_{lk} P_l$ and assume that g_{lk-1} is a polynomial with k terms. Then the Dalgarno-Lewis equation[10] for g_{lk} is

$$g_{lk}'' + 2\left[\frac{1}{r} - 1 \right] g_{lk}' - \frac{l(l+1)}{r^2} g_{lk} = g_{lk-1}$$

$$= \sum_{j=0}^{k-1} d_j r^{l+j} \; . \tag{22}$$

If we assume that g_{lk} has one more power than g_{lk-1} then Eq. (22) takes the following form:

$$\sum_{j=1}^{k} C_j j(j+2l+1) r^{j-2} - 2 \sum_{j=0}^{k} C_j (j+l) r^{j-1} = \sum_{j=0}^{k-1} d_j r^j \; , \tag{23}$$

where C_j are the coefficients of the polynomial of degree k assumed to represent g_{lk}/r^l. Since there are exactly $k+1$ powers of r appearing in Eq. (23) and $k+1$ coefficients C_j to be determined, we can equate like powers of r and derive the following set of recursion relations:

$$\begin{aligned}
&C_1(l+1) - lC_0 = 0 \; , \\
&2C_k(l+k) = -d_{k-1} \; , \\
&C_{j+2}(j+2)(j+3+2l) - 2C_{j+1}(j+l+1) = d_j \\
&\qquad \text{for } 0 \le j < k-1 \; .
\end{aligned} \tag{24}$$

TABLE I. Sum rules $\bar{S}_{l,m}$ for $l=1$ for several expansion lengths N_0. Only odd values of m are displayed since even moments are not needed for the expansion of Eq. (6). The asterisks denote the first entry in each column that is not exact according to the theorem: $m > 2(N_0-1)$.

m	$N_0=3$	$N_0=5$	$N_0=10$	Exact values[a]
1	4.500 000 000			4.5
3	6.645 833 333			6.645 833 333
5	10.756 872 106*	10.761 754 919		10.761 754 919
7	18.071 059 490	18.157 673 463		18.157 673 463
9	30.814 673 369	31.289 676 080*	31.289 711 684	31.289 711 684
11	52.851 869 216	54.557 837 165	54.559 078 118	54.559 078 118
13	90.852 689 618	95.788 396 040	95.799 562 542	95.799 562 542
15	156.310 750 644	168.878 859 561	168.937 240 771	168.937 240 771
17	269.018 922 534	298.497 036 115	298.723 274 206	298.723 274 206
19	463.053 781 434	528.422 459 447	529.149 065 365 57*	529.149 065 365 64
21	797.078 167 150	936.350 896 495	938.406 631 952	938.406 631 962
23	1372.076 626 03	1660.168 358 25	1665.484 322 86	1665.484 323 05
25	2361.885 635 29	2944.579 716 37	2957.447 166 12	2957.447 168 12
35	35 700.115 436	51 793.222 326	52 402.189 016	52 402.192 93
45	539 611.903 34	911 713.017 87	930 197.054 62	930 197.573 05

[a] Obtained using the analytic results of Ref. 7.

TABLE II. Dynamic polarizability $\alpha_l(\omega)$ for $l=1$, evaluated for several expansion lengths. Frequencies are in Rydbergs, and powers of 10 are indicated by superscripts. Asymptotically, $\alpha_1(\omega) \sim 4/\omega^2$.

ω	$N_0=5$	$N_0=10$	$N_0=15$	Exact[a]
0	4.500 000 000			4.5
0.2	4.250 298 265			4.250 298
0.6	2.978 325 25	2.978 325 539		2.978 326
1.0	1.905 385 708	1.905 388 437		1.905 388
1.4	1.258 013 206	1.258 015 644		1.258 016
1.8	$8.745\,688\,320^{-1}$	$8.745\,550\,795^{-1}$	$8.745\,550\,799^{-1}$	$8.745\,551^{-1}$
2.0	$7.424\,633\,450^{-1}$	$7.424\,407\,521^{-1}$	$7.424\,407\,530^{-1}$	$7.424\,407^{-1}$
2.8	$4.245\,686\,268^{-1}$	$4.245\,466\,115^{-1}$	$4.245\,466\,034^{-1}$	$4.245\,466^{-1}$
3.6	$2.719\,793\,245^{-1}$	$2.719\,919\,962^{-1}$	$2.719\,919\,937^{-1}$	$2.719\,919^{-1}$
5	$1.482\,096\,367^{-1}$	$1.482\,515\,864^{-1}$	$1.482\,516\,637^{-1}$	$1.482\,516^{-1}$
7	$7.804\,209\,068^{-2}$	$7.806\,734\,823^{-2}$	$7.806\,725\,510^{-2}$	$7.806\,725^{-2}$
9	$4.793\,537\,772^{-2}$	$4.794\,143\,961^{-2}$	$4.794\,121\,430^{-2}$	$4.794\,121^{-2}$
12	$2.727\,878\,816^{-2}$	$2.727\,338\,352^{-2}$	$2.727\,334\,058^{-2}$	$2.727\,334^{-2}$
16	$1.545\,734\,825^{-2}$	$1.545\,045\,355^{-2}$	$1.545\,065\,744^{-2}$	$1.545\,065^{-2}$
20	$9.929\,116\,688^{-3}$	$9.923\,874\,603^{-3}$	$9.924\,101\,249^{-3}$	$9.924\,092^{-3}$
24	$6.909\,622\,835^{-3}$	$6.905\,982\,104^{-3}$	$6.906\,137\,649^{-3}$	$6.906\,132^{-3}$
50	$1.598\,086\,094^{-3}$	$1.597\,671\,933^{-3}$	$1.597\,631\,269^{-3}$	$1.597\,637^{-3}$
100	$3.998\,793\,861^{-4}$	$3.998\,473\,640^{-4}$	$3.998\,376\,064^{-4}$	$3.998\,364^{-4}$

[a] Reference 6.

TABLE III. van der Waals coefficients in Rydbergs, evaluated by the pseudostate method for varying expansion lengths. C_j are the usual coefficients of R^{-j} in the long-range H-H potential, while D and G are nonadiabatic and energy-dependent coefficients defined in Ref. 3 and Eq. (3). The higher multipoles required for $j=8$ and 10 were evaluated individually by diagonalizing H_0 using basis functions of the appropriate l. They could also have been obtained[a] from the dipole values by invoking the invariance of H_0 under the group 0_4.

	$N_0=3$	$N_0=5$	$N_0=10$	$N_0=15$
C_6	12.996 887 966	12.998 050 710	12.998 053 410 66	12.998 053 410 811 3
C_8	248.773 127 44	248.798 088 99	248.798 167 164 7	248.798 167 167 241
C_{10}	6570.997 258 7	6571.654 479 1	6571.656 829 885	6571.656 829 934 80
D	7.400 246 889 4	7.398 630 690 9	7.398 625 218 328	7.398 625 218 232 3
G	4.356 966 680 5	4.356 498 437 8	4.356 504 821 206	4.356 504 821 254 09

[a] Reference 13.

Thus we see that the system of equations is consistent. To complete the proof we note that the correct two-term expression for g_1 results from the above equations with the potential $g_{l0}=V_l=2r^l$, and our assertion about the form of successive G_{lk} is proven. It follows that the pseudostate method with N_0 terms will give $S_{l,m}$ exactly up to $m=2N_0-2$.

Finally, we assert that the values given for the dynamic polarizabilities are the analytic continuation of the power series discussed here and that the exactness of the first terms of that series should also lead to high accuracy in the analytic continuation. Then from the dynamic polarizabilities we obtain the vdW coefficients with equally high accuracy. An obvious weak point in this argument concerns the remaining, higher coefficients whose inexactness could threaten the accuracy of the vdW coefficients. But since the pseudostates are obtained through a variational calculation they approach the actual hydrogenic states as N_0 increases. For fairly modest values of N_0 the lowest few pseudostates are quite close to the first few states of hydrogen. As m increases the lower values of N dominate since $\Delta(Nl)$ becomes raised to the power of m. Eventually, only the lowest few states are needed to evaluate $S_{l,m}$; for N_0 large enough, then, we can assure the adequate representation of all coefficients in the power series. In addition, for very high frequencies there are asymptotic forms of α_l and β_{lk} which involve only $\bar{S}_{l,0}$ and $\bar{S}_{l,-1}$; these will be shown to be exact in the Appendix.

IV. NUMERICAL RESULTS AND CONCLUSIONS

In this section we will present sample results, illustrating numerically the mathematical statements made above. The prediagonalization of H_0 was carried out with the use of quadruple precision on the IBM 3081 computer. This enabled us to avoid the loss of accuracy experienced by Martin[5] when long expansions ($N_0>10$) were used. The details are otherwise identical to the work described in Ref. 5.

In Table I we give a series of values for the odd-order dipole[12] sum rules S_{1m} that are needed in the expansions of Eq. (6), computed with different values of the expansion length N_0. These are compared with the values obtained from the exact expression derived by Au.[7] The perfect agreement up to order $m=2(N_0-1)$ is evident, and the good agreement beyond this point is also clearly shown.

In Table II we show representative values of the dynamic dipole[12] polarizability $\alpha_1(\omega)$ for a wide range in ω. These are computed for three different expansion lengths and are compared with the values obtained using an exact analytical expression in Ref. 6. The agreement is very good, even for $N_0=5$, but for $N_0=15$ it is really remarkably good. Note also that for the higher values of ω the asymptotic expression $4/\omega^2$ is also quite good. In the evaluation of the vdW coefficients from α and β the lower frequencies dominate, and our approximation is best in that region.

Finally, in Table III we give several different vdW coefficients for three different values of N_0 to display the rate of convergence. These include the usual dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole coefficients C_6, C_8, and C_{10}, respectively. In addition, we show the convergence of the nonadiabatic coefficients D and G needed to take into account the finite mass of the atoms.[3] Note that all these coefficients are evaluated directly, from the pseudostate equivalents of Q_k [Eq. (1)], not by integrating over the dynamic polarizabilities.[6]

We have thus completed our demonstration of the interesting properties of the pseudostate expansion technique for hydrogenic systems and have shown why its convergence is so rapid and efficient. It seems that this method deserves to be even better known and applied to still more computations involving summation over intermediate states.

ACKNOWLEDGMENTS

We thank Dr. A. K. Bhatia for his aid in programming and carrying out many of the numerical computations reported here. C. K. Au acknowledges support for this work under National Science Foundation (NSF) Grants No. PHY-85-10642 and No. PHY-87-10118.

APPENDIX

A slightly different technique is needed to prove that the pseudostate expansion yields exact values for the two sums $S_{l,0}$ and $S_{l,-1}$, since these are not in the form of second-order perturbation sums. To convert them into the standard form we begin with $S_{l,-1}$,

$$S_{l,-1}=\sum_n \langle 1s \mid V_l \mid nl\rangle\langle nl \mid V_l \mid 1s\rangle\Delta(nl)$$

$$\text{where } V_l=2r^lP_l\ . \quad \text{(A1)}$$

If we define the function W_l as the solution of the equation

$$[H_0,V_l]\mid 1s\rangle = W_l \mid 1s\rangle\ , \quad \text{(A2)}$$

then $S_{l,-1}$ can be written in the form

$$S_{l,-1}=\sum_n \frac{\langle 1s \mid W_l \mid nl\rangle\langle nl \mid W_l \mid 1s\rangle}{\Delta(nl)}\ , \quad \text{(A3)}$$

which is in the standard form; the pseudostate expansion technique can be applied as before. The solution to Eq. (A2) is $W_l=4lr^{l-1}P_l$.

To complete the proof of exactness we need only show that the form of basis functions defined in Eq. (7) is adequate to represent the wave function. To show this, we note that Eq. (A2) is the Dalgarno-Lewis equation[10] corresponding to the perturbation sum in Eq. (A3), and, therefore, the perturbed wave function is $V_l \mid 1s\rangle$. This has just the form of the first term of the pseudostate basis. Therefore $S_{l,-1}$ will be exact for $N_0>0$, and $S_{l,0}$ is obtained from the normalization in the usual way.

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