Long-range dispersion interactions. III: Method for two homonuclear atoms

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(Received 12 August 2007; published 12 December 2007)

A procedure for systematically evaluating the long-range dispersion interaction between two homonuclear atoms in arbitrary *LS* coupled states is outlined. The method is then used to generate dispersion coefficients for a number of the low-lying states of the Na and Mg dimers.

DOI: 10.1103/PhysRevA.76.062703 PACS number(s): 34.20.Cf, 31.25.Jf, 31.15.Pf, 32.10.Dk

I. INTRODUCTION

In this paper a systematic approach to the calculation of the long-range interactions between two homonuclear atoms in arbitrary atomic states is presented. For two spherically symmetric atoms in their ground states, the interaction can be written [1,2], e.g.,

$$V(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \cdots . \tag{1}$$

The C_n parameters are the dispersion coefficients while R is the distance between the two nuclei. The procedures for determining the dispersion coefficients for identical atoms in two spherically symmetric states are known and there has been a lot of activity in calculating the van der Waals coefficients for such atoms [3–9].

When one of the atoms is in a state with nonzero angular momentum the situation becomes more complicated. In the first case, the dispersion coefficient depends on the angular momentum projection of the state. In the second case, there is a possibility of excitation transfer between the two atoms leading to what is usually termed the resonant van der Waals interaction. This results in additional terms appearing in the interaction potentials, e.g., the existence of a term inversely proportional to R^3 when one of the atoms is in a P state and the other is in an S state.

The purpose of the present paper is to describe a procedure for the calculation of the C_n dispersion parameters for homonuclear atoms in arbitrary states. An examination of some earlier work on this topic gives one the impression that the theoretical formalisms for systems involving nonzero angular momentum were developed in an *ad hoc* fashion with expressions for different configurations derived on a case by case basis [5,10–14]. Previously, the most sophisticated treatments were the tensorial approaches developed by Ovsiannikov [15] and Santra and Greene [16]. The present study describes a general procedure which makes use of previous results derived to describe the dispersion interaction between two heteronuclear atoms [17]. Once the formalism is presented, it is applied to the calculation of the dispersion interaction for a number of alkali-metal and alkaline-earth metals atoms.

II. THEORETICAL DEVELOPMENT

A. Theoretical overview

The approach used to generate the dispersion coefficients is based on the work of Dalgarno who originally derived expressions in terms of oscillator strength sum rules [1,2]. This reduced the calculation of the C_n parameters for two spherically symmetric atoms to summations over the products of the absorption oscillator strengths (originating in the ground state) divided by an energy denominator. The sums should include contributions from all discrete and continuum excitations. In practice a pseudostate representation is used which gives a discrete representation of the continuum [6,17,18]. The sum over oscillator strengths needs to be rewritten in terms of a sum over the reduced matrix elements of the electric multipole operator in cases where one (or both) of the atoms is in a state with $L > 0$ [17].

The major part of any calculation involves the generation of the lists of reduced transition matrix elements for the two atomic states. This involves quite lengthy calculations to generate the excitation spectrum of the pseudostate representation. It is then a relatively straightforward calculation to use the procedure outlined in the present paper to process the lists of matrix elements and generate the dispersion coefficients.

This section presents the algebraic results that are needed in the evaluation of the sum rules in their most general form.

B. Matrix element evaluation

The general expression for the long-range interaction between two atoms has contributions from both first-order and second-order perturbation theory [19]. There are three classes of interaction that arise. In the first case, there is the interaction that arises from second-order perturbation theory which is always present. This interaction can be written as

$$V_1(R) = -\sum_{s=1} \frac{C_{2s+4}}{R^{2s+4}}, \quad \ldots . \tag{2}$$

In the second case, there is a first-order interaction that arises when both atomic states have nonzero orbital angular momentum. This term can be written as

$$V_2(R) = -\sum_{s=1}^{L_a+L_b-1} \frac{C_{2s+3}}{R^{2s+3}}, \quad \ldots . \tag{3}$$

The number of terms in this sum are finite and depends on the angular momentum of the individual atoms. The simplest example of such an interaction is the quadrupole-quadrupole interaction that occurs between two atoms in a P state.

The final interaction occurs because the two atoms are identical (i.e., all the nonorbital quantum numbers are the same). This means that excitation transfer between the two atoms is possible as a first-order interaction. This interaction is sometimes called the resonant van der Waals interaction, and is written as

$$V_3(R) = -\sum_{s=|L_a-L_b|}^{|L_a+L_b|} \frac{C_{2s+1}}{R^{2s+1}}. \tag{4}$$

The range of allowed multipoles depends on the orbital angular momentum quantum numbers (L_a and L_b) of the two atoms. Once again the number of terms in this sum are finite and depend on the angular momentum of the individual atoms. The simplest example of such an interaction is the C_3/R^3 dipole interaction that occurs when one atom is in an S state and the other is in a P state.

The basic strategy adopted in the present work is to first generate the basis of all allowable states in an atomic representation. Next, the general expressions for the first and second interactions between those states are developed. The asymptotic molecular states are then derived by diagonalizing the Hamiltonian matrix for the multipole with the smallest inverse power of internuclear distance. The dispersion coefficients can then be evaluated by simply computing the matrix elements of the first- and second-order interactions in the molecular representation.

All expressions are given for the case of two atoms each with a single active electron. These expressions can be trivially extended to the more general case since all atomic structure information is encapsulated in the reduced matrix elements.

C. Multipole expansion

The dispersion interaction operator in the asymptotic region, $R \gg a_0$, may be presented in the form of expansion in power series of R^{-1} [20],

$$V(\mathbf{R}) = \sum_{k=1}^{\infty}\sum_{k'=1}^{\infty} \frac{v_{kk'}(\hat{\mathbf{n}})}{R^{k+k'+1}}, \tag{5}$$

where

$$v_{kk'}(\hat{\mathbf{n}}) = (-1)^{k'}\left(\frac{(2K)!}{(2k)!\,(2k')!}\right)^{1/2} \times (\mathbf{C}^K(\hat{\mathbf{n}}) \cdot [\mathbf{Q}^k(\mathbf{r}_a) \times \mathbf{Q}^{k'}(\mathbf{r}_b)]^K), \tag{6}$$

where $K=k+k'$, $\mathbf{Q}^k(\mathbf{r})=r^k\mathbf{C}^k(\mathbf{r})$ is the operator of the atomic 2^k-pole electric moment, and the unit vector $\hat{\mathbf{n}}=\mathbf{R}/R$ points from the first atom (a) to the second atom (b). The $\mathbf{C}^k(\theta,\varphi)$ and $\mathbf{C}^K(\hat{\mathbf{n}})$ are the spherical tensors [21] of angular variables of the atomic electron's position vector $\mathbf{r}=\{r,\theta,\varphi\}$ and those of the interatomic unit vector $\hat{\mathbf{n}}$, correspondingly. Defining the quantization axis in the $\hat{\mathbf{n}}$ direction simplifies Eq. (6) to

$$\begin{aligned} v_{kk'}(\hat{\mathbf{n}}) &= (-1)^{k'}\left(\frac{(2K)!}{(2k)!\,(2k')!}\right)^{1/2} [\mathbf{Q}^k(\mathbf{r}_a) \times \mathbf{Q}^{k'}(\mathbf{r}_b)]_0^K \\ &= (-1)^{k'}\left(\frac{(2K)!}{(2k)!\,(2k')!}\right)^{1/2} \\ &\quad \times \sum_{\mu} \langle k-\mu k'\mu|K0\rangle Q_{-\mu}^k(\mathbf{r}_a) Q_{\mu}^{k'}(\mathbf{r}_b). \end{aligned} \tag{7}$$

D. Atomic representation

The zeroth-order basis function for two like atoms a and b in states with angular momenta l_a and l_b, with magnetic projections m_a and m_b, and a total magnetic quantum number $M=m_a+m_b$ can be written in the product form

$$\Psi(n_a,n_b,m_a,m_b,M) = \Psi_{n_a l_a, m_a}(\mathbf{r}_1)\Psi_{n_b l_b, m_b}(\mathbf{r}_2), \tag{8}$$

where Ψ_{n_a} has an energy eigenvalue of E_{n_a}, and Ψ_{n_b} has an energy eigenvalue of E_{n_b}. The electronic and nuclear spin quantum numbers of a and b should be the same. These basis states occur as degenerate pairs when the (n_a,l_a,m_a) and (n_b,l_b,m_b) quantum numbers are different. This second degenerate basis state is

$$\Psi(n_b,n_a,m_b,m_a,M) = \Psi_{n_b l_b, m_b}(\mathbf{r}_1)\Psi_{n_a l_a, m_a}(\mathbf{r}_2). \tag{9}$$

E. First-order interaction

It is normal to treat the first-order interaction as two cases. There is the direct case, and there is the case where the states have their electron coordinates interchanged. The computational approach adopted makes no distinction between these cases.

Accordingly, the first-order interaction is initially evaluated between two atomic states, the $\Psi(n_a,n_b,m_a,m_b,M)$ and $\Psi(n_c,n_d,m_c,m_d,M)$ basis functions. The electron-electron operator, Eq. (5), conserves M but not m_a or m_b. The general matrix element is written as

$$V^{(1)}_{m_a m_b m_c m_d} = \sum_{kk'\mu} \frac{(-1)^{k'}}{R^{K+1}}\left(\frac{(2K)!}{(2k)!(2k')!}\right)^{1/2} \langle k-\mu k'\mu|K0\rangle \times \langle n_a l_a m_a n_b l_b m_b|Q_{-\mu}^k Q_{\mu}^{k'}|n_c l_c m_c n_d l_d m_d\rangle \tag{10}$$

which is expressed most conveniently as

$$\begin{aligned} V^{(1)}_{m_a m_b m'_a m'_b} &= \sum_{kk'} \frac{(-1)^{k'}}{R^{K+1}}\left(\frac{(2K+1)!}{(2k)!(2k')!}\right)^{1/2} \\ &\quad \times \langle n_a l_a\|r^k\mathbf{C}^k\|n_c l_c\rangle\langle n_b l_b\|r^{k'}\mathbf{C}^{k'}\|n_d l_d\rangle \\ &\quad \times \sum_{\mu}(-1)^{l_a-m_a+l_b-m_b}\begin{pmatrix} l_a & k & l_c \\ -m_a & -\mu & m_c \end{pmatrix} \\ &\quad \times \begin{pmatrix} l_b & k' & l_d \\ -m_b & \mu & m_d \end{pmatrix}\begin{pmatrix} k & k' & K \\ -\mu & \mu & 0 \end{pmatrix}. \end{aligned} \tag{11}$$

The two possibilities that occur are the $(n_c=n_a, n_d=n_b)$ and the $(n_c=n_b, n_d=n_a)$ cases. The first case can be regarded as the direct term and the second case can be regarded as the exchange case.

The matrix element for the direct term which occurs between the $\Psi(n_a,n_b,m_a,m_b,M)$ and $\Psi(n_a,n_b,m_a',m_b',M)$ states is zero if one of the atoms is in an S state and the first configuration leading to a nonzero quadrupole interaction is the P-P case. The C_{K+1} coefficients are obtained from Eq. (11) by setting $n_c=n_a$, $n_d=n_b$ and multiplying by $-R^{K+1}$.

The exchange first-order interaction occurs between the $\Psi(n_a,n_b,m_a,m_b,M)$ and $\Psi(n_b,n_a,m_b',m_a',M)$ basis functions. The exchange first-order interaction is zero if both of the atoms are in an S state. All other configurations result in a finite matrix element. The first term that arises is a term with $k=|l_a-l_b|$ and $K=2|l_a-l_b|$. The C_{K+1} coefficients are obtained from Eq. (11) by setting $n_c=n_b, n_d=n_a$ and multiplying by $-R^{K+1}$. When one atom is in an S state (i.e., $l_a=0$) and the other one is not, the first-order interaction can be expressed in terms of the oscillator strength, e.g.,

$$V_{m_b}^{(1)}=\frac{1}{2R^{2l_b+1}}\frac{(-1)^{l_b-m_b}(2l_b)!}{(l_b+m_b)!(l_b-m_b)!}\frac{f_{n_an_b}^{(l_b)}}{E_{n_b}-E_{n_a}}. \tag{12}$$

In writing Eq. (12), the absorption oscillator strength of multipole k for a transition from $n_a\rightarrow n_b$ has been defined as

$$f_{n_an_b}^{(k)}=\frac{2|\langle\psi_{n_a};L_a||r^k\mathbf{C}^k(\hat{\mathbf{r}})||\psi_{n_b};L_b\rangle|^2\Delta E_{n_bn_a}}{(2k+1)(2L_a+1)}. \tag{13}$$

where $\Delta E_{n_bn_a}=E_{n_b}-E_{n_a}$.

The first-order interaction is the part of the atom-atom interaction with the longest range for many pairs of states and thus determines the asymptotic form of the molecular wave function in those cases.

F. Second-order interaction

For the second-order interaction $V^{(2)}$, the general matrix element in uncoupled form is

$$V^{(2)}_{m_am_bm_a'm_b'}=-\sum_{k_1k_1'\mu_1}\sum_{k_2k_2'\mu_2}\sum_{\substack{n_cm_c\\n_dm_d}}\frac{(-1)^{k_1'+k_2'}}{R^{K_1+K_2+2}}\left(\frac{(2K_1)\,!\,(2K_2)!}{(2k_1)\,!\,(2k_1')\,!\,(2k_2)\,!\,(2k_2')!}\right)^{1/2}\langle n_al_am_an_bl_bm_b|Q^{k_1}_{-\mu_1}Q^{k_1'}_{\mu_1}|n_cl_cm_cn_dl_dm_d\rangle$$
$$\times\frac{\langle n_cl_cm_cn_dl_dm_d|Q^{k_2}_{-\mu_2}Q^{k_2'}_{\mu_2}|n_el_em_en_fl_fm_f\rangle}{E_{n_c}+E_{n_d}-E_{n_a}-E_{n_b}}\langle k_1-\mu_1k_1'\mu_1|K_10\rangle\langle k_2-\mu_2k_2'\mu_2|K_20\rangle. \tag{14}$$

Applying the Wigner-Eckart theorem and collecting terms gives

$$V^{(2)}_{m_am_bm_a'm_b'}=-\sum_{k_1k_1'\mu_1}\sum_{k_2k_2'\mu_2}\sum_{n_cn_d,m_cm_d}\frac{(-1)^{k_1'+k_2'}}{R^{K_1+K_2+2}}\left(\frac{(2K_1+1)\,!\,(2K_2+1)!}{(2k_1)\,!\,(2k_1')\,!\,(2k_2)\,!\,(2k_2')!}\right)^{1/2}\frac{\langle n_al_a||r^{k_1}\mathbf{C}^{k_1}||n_cl_c\rangle\langle n_el_e||r^{k_2}\mathbf{C}^{k_2}||n_cl_c\rangle}{E_{n_c}+E_{n_d}-E_{n_a}-E_{n_b}}$$
$$\times\langle n_bl_b||r^{k_1'}\mathbf{C}^{k_1'}||n_dl_d\rangle\langle n_fl_f||r^{k_2'}\mathbf{C}^{k_2'}||n_dl_d\rangle\begin{pmatrix}l_a & k_1 & l_c\\ -m_a & -\mu_1 & m_c\end{pmatrix}\begin{pmatrix}l_b & k_1' & l_d\\ -m_b & \mu_1 & m_d\end{pmatrix}\begin{pmatrix}l_c & k_2 & l_e\\ -m_c & -\mu_2 & m_e\end{pmatrix}\begin{pmatrix}l_d & k_2' & l_f\\ -m_d & \mu_2 & m_f\end{pmatrix}$$
$$\times\begin{pmatrix}k_1 & k_1' & K_1\\ -\mu_1 & \mu_1 & 0\end{pmatrix}\begin{pmatrix}k_2 & k_2' & K_2\\ -\mu_2 & \mu_2 & 0\end{pmatrix}. \tag{15}$$

The two possibilities that occur are the $(n_e=n_a,n_f=n_b)$ and the $(n_e=n_b,n_f=n_a)$ cases. The first case can be regarded as the direct term and the second case can be regarded as the exchange case. There is no startling difference between the form of the expression for direct and exchange terms, although sum rules in many cases for the direct terms reduce to sums over products of oscillator strengths.

The products of the reduced matrix elements are written with the intermediate states (n_c,n_d) on the right-hand side of the matrix element. They are written in this fashion so that in cases where the choices of n_c, n_d, n_e, n_f cause any reduced matrix element product to simplify to an oscillator strength, then this simplification can be done transparently. This makes the inclusion of the core using the techniques of [17,22] straightforward.

G. Molecular wave functions

The zeroth-order wave function for the combined system a-b for two like atoms a and b, in states with angular momenta l_a and l_b, with a total magnetic quantum number M can be written in the form

$$\Psi^{(0)}(a,b,M)=\sum_{m_a=-l_a}^{+l_a}\sum_{m_b=-l_b}^{+l_b}\delta_{m_a+m_b,M}C_{m_a,M}\Psi(n_am_an_bl_bm_b,M), \tag{16}$$

where Ψ_{n_a} has an energy eigenvalue of E_{n_a}, and Ψ_{n_b} has an energy eigenvalue of E_{n_b}. The expansion constant is $C_{m_a,M}$.

While the symmetry properties of the wave functions can be used to simplify the construction of the Hamiltonian, we prefer to use the symmetry properties of the Hamiltonian to construct the wave functions. This idea is implicit in the m-scheme shell model [23]. Since the Hamiltonian commutes with the available symmetry operators, diagonalizing the Hamiltonian in a basis spanning the entire space of symmetry states will automatically generate wave functions that are eigenstates of the symmetry operators.

As mentioned earlier, for $n_a \neq n_b$ one must include the $\Psi(n_a m_a n_b m_b, M)$ and $\Psi(n_b m_b n_a m_a, M)$ states in the basis. When the Hamiltonian is diagonalized, one finds states in combinations

$$\Psi^{(0)} = \Psi(n_a m_a n_b m_b, M) + \beta \Psi(n_b m_b n_a m_a, M), \qquad (17)$$

where $\beta = \pm 1$ and can be related to the fundamental symmetries of the states by $\beta = (-1)^{l_a + l_b}(-1)^S P$, and S is the total spin, $p = +1$ for even (g) and $p = -1$ for odd (u) molecular states. This symmetry was exploited as a check of program correctness. The van der Waals operator is diagonal in β and cannot connect states with different β. Rather than assuming that the matrix element is diagonal in β, the van der Waals coefficients were evaluated explicitly between all the possible combination of states to check that the C_n coefficients were zero when the states had a different β. This provides a useful diagnostic check into the details of program construction.

When one of the atoms (a) is in an S state and the other is in a different state, one has $m_b = M$ and the zero-order wave function is

$$\Psi^{(0)}(n_a, n_b, M) = \Psi(n_a 0 n_b M, M) + \beta \Psi(n_b M n_a 0, M). \qquad (18)$$

The asymptotic molecular representation in cases when both atoms are in states with nonzero angular momentum can be defined in most cases by diagonalizing the first-order interaction with the lowest multipole.

The practical implementation of the present formalism has a strong computational flavor. All the possible $\Psi(n_a n_b m_a m_b M)$ states of a given M are gathered in the basis. This basis is then used to diagonalize the interaction with the lowest inverse power of R^n. The entire first- and second-order matrix blocks are then constructed between all possible $\Psi(n_a n_b m_a m_b M)$ basis states, then the contractions over the linear expansion coefficients are done to generate the symmetry-adapted dispersion coefficients. There are only two matrix elements that are computed, namely Eqs. (11) and (15). All possible sums over the indices k_1, k_1', μ_1, and so on are automatically done using selection rules while accumulating all terms of a given K or $(K_1 + K_2)$.

The computer program was tested by repeating some earlier calculations of the dispersion coefficients for the Li [26] and He [27–29] dimers. The lists of transition matrix elements used by these previous works were input into the program developed to use the present formalism. Naturally, these earlier dispersion coefficients were reproduced.

H. Feshbach description

There is one aspect about existing discussions of the van der Waals interaction [12,17,26,27,30]) that is not entirely satisfactory when both atoms are in states with $\ell > 0$. The existence of a number of different molecular states which have the same energy raises the possibility of both atoms experiencing an excitation to a energetically degenerate state resulting in the energy denominator of the intermediate state expansion being zero. Marinescu *et al.* [12] resorted to degenerate perturbation theory as a means to eliminate unwanted zeros for the gerade and ungerade asymptotically degenerate states for homonuclear atoms. While this procedure is satisfactory when one of the atoms is in a spherically symmetric state, it did not completely resolve all the issues that would arise if both atoms were in states with $\ell > 0$.

The issues to be resolved are best discussed by reference to a specific example, namely the case where $l_a = l_b = 1$. Marinescu *et al.* defined the zeroth-order molecular wave function for the Σ states by the diagonalization of the first-order quadrupole interaction. This ensures that the matrix element of the quadrupole operator connecting two distinct degenerate states with positive reflection symmetry about a plane containing the nuclear axis will be zero (the state with negative reflection symmetry automatically has a matrix element of zero with states of positive reflection symmetry). Thus the energetically degenerate double excitation via quadrupole transitions can be removed from the perturbation expansion for C_{10}. However, the molecular representation that diagonalizes the quadrupole interaction does not necessarily diagonalize the C_6 or C_8 interaction. There are off-diagonal second-order terms connecting two of the Σ states [17]. The existence of an off-diagonal term in C_6 has not even been mentioned in some earlier work [12,26,27,30]. Diagonalizing the C_6 operator will lead to a new molecular representation that will not necessarily diagonalize the quadrupole operator. This raises the possibility of a zero occurring in the energy denominator for C_{10} when $k_1 = k_2 = k_1' = k_2' = 2$.

The way forward is to make use of the Feshbach formalism which divides all possible channels into P space and Q space [31]. Channels or states in P space are included explicitly and interactions between P-space states are therefore included to all orders. The interactions of Q-space states with those in P space are handled by means of an optical potential. In practical calculations, the interaction of Q space with P space is often handled using perturbation theory. Santra and Greene used the Feshbach partitioning in their recent tensorial analysis of the long-range interaction between two metastable alkaline-earth atoms [16]. Prior to this, Dalgarno and Derevianko used similar ideas (without referencing the Feshbach partitioning) in an analysis of the interactions between metastable rare gas atoms [32].

This picture provides a formal setting that is well suited to the description of van der Waals interactions. The P space would constitute the set of asymptotically degenerate atomic states of a particular molecular configuration. The Q space would consist of those two-atom states used in the calculation of the van der Waals interaction. As long as the interactions between the P-space states are calculated with the full interaction [in this case the asymptotic interaction of Eq. (5)] then this partitioning eliminates the possibility of a zero in the energy denominator for the van der Waals intermediate state summation. Accordingly, a diagonalization of the first-order interaction plus the second-order interaction connect-

TABLE I. The dispersion coefficients for the 3*s*-3*s* and 3*s*-4*s* combinations of sodium. Data by other groups are identified by the citation in the first column (MBPT means many-body perturbation theory [24,25] while MP means model potential [3,10]). The numbers in the square brackets denote powers of 10.

System	β	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
3*s*-3*s*		1.563[3]	1.159[5]	1.134[7]
3*s*-3*s* MBPT		1.564[3]	1.160[5]	1.13[7]
3*s*-3*s* MP		1.472[3]	1.119[5]	1.107[7]
3*s*-4*s*	+1	2.568[4]	5.600[6]	1.688[9]
3*s*-4*s*	−1	1.477[4]	4.267[6]	1.412[9]
3*s*-4*s* MP	+1	2.519[4]	5.418[6]	1.650[9]
3*s*-4*s* MP	−1	1.430[4]	4.146[6]	1.374[9]

ing all *P*-space states can be formally justified.

As an example, consider again the case $l_a = l_b = 1$. Generating the C_5, C_6, C_8, etc., coefficients for the two Σ states with off-diagonal C_6, etc., terms is sufficient to define long-range interaction. The interaction matrix between these two Σ states can be constructed from the diagonal and off-diagonal C_n coefficients at any internuclear radius. Diagonalization of the resulting 2×2 matrix will then give the long-range interaction.

A Feshbach partitioning could also provide a very convenient analysis tool with which we analyze the long-range behavior of molecular configurations with additional complications. For example, the manifolds of energetically close states that occur when the spin-orbit and/or hyperfine energy differences are included can be regarded as comprising an enlarged *P* space while those states included for the second-order interaction can be regarded as comprising *Q* space.

III. SODIUM DIMER

The calculational technology is first applied to the determination of the long-range interactions between two sodium atoms. All the dispersion coefficients were computed by first diagonalizing the semiempirical Hamiltonian [6,33–36] in a large mixed Laguerre-type orbital and Slater-type orbital basis set [6]. Next, various sum rules involving oscillator strengths or reduced matrix elements were summed over the set of physical states and pseudostates.

The calculations for sodium used the wave functions described in an earlier calculation of dispersion coefficients of sodium–rare-gas combinations [17,37]. These wave functions represented some minor improvements on wave functions used to describe the dispersion interactions of ground state sodium [6,8]. The reduced matrix elements of the multipole operators were computed with a modified operator that allowed for polarization corrections [6,38,39].

The results of the stand-alone structure calculations are lists of reduced matrix elements for all the valence states of interest. The impact of excitations from the core were included using a procedure outlined previously [17,22,26].

The dispersion coefficients between the 3*s* state and other low-lying states of Na listed are in Tables I–III. Also listed in the tables are the model potential (MP) values generated by Marinescu and co-workers [3,10] and the values generated from many-body perturbation theory (MBPT) calculations [25]. Positive C_n values indicate attractive interactions while negative values indicate repulsive interactions.

As noted previously, there is better than 1% agreement between the present and MBPT calculations [6,8] for the ground state dimer. This agreement does not extend to the model potential calculations. The MP calculation does not include the impact of the core and which results in their

TABLE II. The dispersion coefficients between the 3*s*-*np* atoms of Na_2. The model potential (MP) values are taken from the calculations of Marinescu and Dalgarno [10]. The numbers in the square brackets denote powers of 10.

System	β	C_3 (a.u.)	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
3*s*-3*p* Σ	+1	12.44	4.232[3]	7.338[5]	1.109[8]
3*s*-3*p* Σ	−1	−12.44	4.232[3]	2.162[6]	3.350[8]
3*s*-3*p* Π	+1	−6.221	2.732[3]	2.198[5]	2.167[7]
3*s*-3*p* Π	−1	6.221	2.732[3]	8.838[4]	1.871[6]
3*s*-3*p* Σ MP	+1	12.26	4.094[3]	7.025[5]	
3*s*-3*p* Σ MP	−1	−12.26	4.094[3]	2.120[6]	
3*s*-3*p* Π MP	+1	−6.128	2.636[3]	2.171[5]	
3*s*-3*p* Π MP	−1	6.128	2.636[3]	8.559[4]	
3*s*-4*p* Σ	+1	0.0929	4.923[4]	4.266[7]	2.342[10]
3*s*-4*p* Σ	−1	−0.0929	4.923[4]	4.473[7]	2.389[10]
3*s*-4*p* Π	+1	−0.0464	2.667[4]	1.491[6]	3.472[8]
3*s*-4*p* Π	−1	0.0464	2.667[4]	1.641[6]	3.217[8]
3*s*-4*p* Σ MP	+1	0.0843	4.806[4]	8.368[7]	
3*s*-4*p* Σ MP	−1	−0.0843	4.806[4]	8.558[7]	
3*s*-4*p* Π MP	+1	−0.0422	2.602[4]	1.548[7]	
3*s*-4*p* Π MP	−1	0.0422	2.602[4]	1.558[7]	

TABLE III. The dispersion coefficients for the 3s-3d state of the sodium dimer. The model potential (MP) values are taken from the calculations of Marinescu and co-workers [10]. The numbers in the square brackets denote powers of 10.

System	β	C_5 (a.u.)	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
3s-3d Σ	+1	−588.4	4.141[4]	1.996[7]	9.648[9]
3s-3d Σ	−1	588.4	1.919[4]	1.552[7]	8.481[9]
3s-3d Π	+1	393.3	1.891[4]	4.358[6]	5.099[8]
3s-3d Π	−1	−393.3	3.371[4]	6.019[6]	6.592[8]
3s-3d Δ	+1	−98.07	1.805[4]	−8.159[5]	−5.722[6]
3s-3d Δ	−1	98.07	1.065[4]	−5.979[5]	−2.202[6]
3s-3d Σ MP	+1	−578.3	4.059[4]		
3s-3d Σ MP	−1	578.3	1.867[4]		
3s-3d Π MP	+1	385.5	1.842[4]		
3s-3d Π MP	−1	−385.5	3.303[4]		
3s-3d Δ MP	+1	−96.4	1.766[4]		
3s-3d Δ MP	−1	96.4	1.035[4]		

values being too small by amounts between 2% and 5% [6].

The dispersion coefficients for the 3s-4s case listed in Table I once again result in the present calculations giving dispersion coefficients that are about 2%–3% larger than the MP values. The likely reason for the slight difference is the omission of the core from the MP calculation.

The dispersion coefficients for the 3s-3p and 3s-4p configurations of the sodium dimer are listed in Table II. The dispersion coefficients for the 3s-3p configuration are generally a couple of percent larger than the MP results of Marinescu and Dalgarno [10], presumably due to the present inclusion of the core. This level of agreement does not occur for the 3s-4p configuration. The present dispersion coefficients are about one-half the size of the MP results for the Σ symmetry. It should be noted that major discrepancies with MP dispersion coefficients also occurred for the 2s-3p configuration of lithium [26].

The dispersion coefficients between the 3s and 3d states of two sodium atoms are given in Table III. The only previous calculation that had been done was the MP calculation which only reported C_6 values. Once again the inclusion of the core gave C_6 values slightly larger than the MP values.

There are also large discrepancies with the dispersion coefficients of Marinescu [12] for the 3p-3p configuration listed in Table IV. While the dispersion coefficients for the two Π symmetries and the Δ symmetry agree within a few percent, this is not the case for the three states of Σ symmetry. The wave functions for the Σ_1 states change sign upon reflection through a plane containing the two nuclei, while the Σ_2 and Σ_3 states do not change sign. The dispersion interaction for the Σ_2 and Σ_3 states is most properly determined by diagonalizing the 2×2 interaction matrix at each internuclear separation.

There is a big difference in C_6 for the Σ_3 state, the present value of −9965 a.u. being much more negative than the value of Marinescu. A similar discrepancy existed for the same molecular state in the Li dimer [12]. Further, there also exist orders of magnitude discrepancies in C_8 for the Σ_1 and Σ_3 states. It has been noted that two of the formulas used by Marinescu to calculate C_8 had mistakes [26]. Given that the program used to process the file of transition matrix elements into dispersion coefficients has previously been validated against independent calculation, the most likely source of error lies in the Marinescu calculation.

IV. MAGNESIUM DIMER

The alkaline-earth dimers have weakly bound van der Waals ground states and strongly bound excited states. This causes the spectral transitions to appear as broad continua that are shifted to the red of the corresponding atom lines. Such transitions are well suited to laser applications [44]. In addition there has been a good deal of interest in the alkaline-earth dimers due to cold atom applications [45–47].

TABLE IV. The dispersion coefficients for the 3p-3p state of the sodium dimer. The model potential (MP) values are taken from the calculations of Marinescu [12]. The Σ_2-Σ_3 row gives the off-diagonal dispersion coefficients between the two states. The numbers in the square brackets denote powers of 10.

Symmetries	C_5 (a.u.)	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
Σ_1	0	4.337[3]	−4.880[4]	−9.200[6]
Σ_1 MP	0	4.270[3]	−5.181[7]	
Σ_2	0	1.748[3]	9.739[6]	7.549[8]
Σ_2 MP	0	1.816[3]	9.236[6]	
Σ_3	−2.330[3]	−9.965[3]	1.098[6]	3.702[9]
Σ_3 MP	−2.289[3]	−396.6	1.507[6]	
Σ_2-Σ_3	0	1.064[3]	−3.750[6]	−3.076[9]
Π_1	1.553[3]	5.504[3]	3.234[6]	−6.970[8]
Π_1 MP	1.526[3]	5.431[3]	3.194[6]	
Π_2	0	1.831[3]	1.029[7]	6.472[8]
Π_2 MP	0	1.910[3]	1.015[7]	
Δ	−388.3	2.501[3]	4.067[6]	−4.824[8]
Δ MP	−381.4	2.509[3]	4.001[6]	

TABLE V. Theoretical and experimental energy levels (in hartree) of some of the low-lying states of the Mg atom. The energies are given relative to the energy of the ionized core. The experimental energies (taken from [40,41]) for the doublet states are averages with the usual $(2J+1)$ weighting factors. The dipole, quadrupole, and tensor polarizabilities (for dipole excitations) are also listed. Other calculations include MBPT calculations [42] and TDGI calculations [43]. The numbers in the square brackets denote powers of 10.

	Energy (a.u.)		α_1 (a.u.)		$\alpha_{1,2LL}$ (a.u.)		α_2 (a.u.)	
State	Theory	Experimental	Present	Other	Present	Other	Present	Other
$3s^2\ {}^1S^e$	−0.833522	−0.833533	71.35	71.33 MBPT, 74.0 TDGI			811.4	812 MBPT
$3s3p\ {}^1P^o$	−0.673789	−0.673824	293.1	311 TDGI	−111.4	−134.0 TDGI	6.946[3]	
$3s4s\ {}^1S^e$	−0.635564	−0.635314	1.488[3]	1.131[3] TDGI			2.371[5]	
$3s3d\ {}^1D^e$	−0.622101	−0.622102	1.236[3]		−833.6		1.030[4]	
$3s4p\ {}^1P^o$	−0.608655	−0.608690						
$3s3p\ {}^3P^o$	−0.733629	−0.733788	101.5	90.7 TDGI	−14.15	−19.64 TDGI	1.445[3]	
$3s4s\ {}^3S^e$	−0.645827	−0.645821	1.431[3]	1.437[3] TDGI			1.035[5]	
$3s3d\ {}^3D^e$	−0.615014	−0.615021	−3.200[4]		3.276[4]		9.661[4]	
$3s4p\ {}^3P^o$	−0.615609	−0.615519						

However, there has been comparatively little effort in characterizing the potential curves of the excited states of the alkaline-earth dimers despite the many determinations of the potential surface for the ground states. The ground state potential of the magnesium dimer has been the subject of many investigations [44,48–50]. There have been few calculations of the excited states [44] and there has only been a single calculation of the dispersion coefficients for the excited states [43]. The present calculations of the Mg_2 dispersion coefficients will permit an accurate description of the long-range behavior of the most important excited states.

A. Structure of the ground and excited states

The configuration interaction (CI) calculations that generated the Mg physical states and the L^2 pseudostates are very similar to those used to determine the dispersion parameters of the Mg ground state and the metastable ${}^3P^o$ [6,22,35]. The major difference between present calculations and the earlier calculations is that the orbital basis is somewhat larger. There were a total of 156 valence orbitals with a maximum orbital angular momentum of $\ell=6$. The dimensions of the CI basis for the different symmetries varied from 1500 to 4800.

The use of such a large orbital basis resulted in wave functions and energies for the low-lying states that were close to convergence. The effective Hamiltonian for the two valence electrons used a Hartree-Fock wave function for the Mg ground state. The direct and exchange interactions of the valence electrons with the core were calculated exactly. A semiempirical polarization potential was also added to the core potential. This potential included both one-body and two-body terms. The cutoff parameters of the polarization potential were fixed by tuning low-lying states of Mg^+ to the experimental energies. Some additional small adjustments to the cutoff parameters were made for some symmetries by

TABLE VI. Theoretical and experimental values of the oscillator strengths for selected transitions of the Mg atom. The other theoretical f values were taken from the CI calculation of Moccia and Spizzo [51], the TDGI calculation [43] and the MCDF compilation [52]. The experimental data are taken from various sources.

		Other theory			
Transition	Present CI	CI	TDGI	MCDF	Experiment
$3s^2\ {}^1S^e \rightarrow 3s3p\ {}^1P^o$	1.732	1.761	1.766	1.719	1.75(8) (Ref. [53])
$3s^2\ {}^1S^e \rightarrow 3s4p\ {}^1P^o$	0.1058	0.1154	0.187	0.1136	0.1070(19) (Ref. [54])
$3s3p\ {}^1P^o \rightarrow 3s4s\ {}^1S^e$	0.1523	0.1553	0.173	0.1555	0.15(1) (Ref. [55])
$3s3p\ {}^1P^o \rightarrow 3s3d\ {}^1D^e$	0.2473	0.2069	0.337	0.247	0.24(2) (Ref. [55])
$3s3p\ {}^3P^o \rightarrow 3s4s\ {}^3S^e$	0.1384	0.1354	0.136	0.137	0.139(3) (Ref. [56]), 0.135(12) (Ref. [57]), 0.117(9) (Ref. [58])
$3s3p\ {}^3P^o \rightarrow 3s3d\ {}^3D^e$	0.6249	0.6383	0.625	0.599	0.55(4) (Ref. [53]), 0.603(8) (Ref. [57]),
$3s3p\ {}^3P^o \rightarrow 3p^2\ {}^3P^e$	0.6173	0.6336			0.62(4) (Ref. [59])

TABLE VII. The dispersion coefficients for the $3s^2$-$3sns$ combinations of magnesium. Values of C_6 for all states are from TDGI calculations [43] while MBPT results [42] are given for the ground state. The numbers in the square brackets denote powers of 10.

System	β	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
$3s^2$-$3s^2$		629.4	4.151[4]	2.809[6]
$3s^2$-$3s^2$ MBPT		627	4.15[4]	2.76[6]
$3s^2$-$3s^2$ TDGI		674		
$3s^2$-$3s4s$ $^1S^e$	+1	7.263[3]	1.573[6]	3.995[8]
$3s^2$-$3s4s$ $^1S^e$	−1	5.584[3]	1.334[6]	3.615[8]
$3s^2$-$3s4s$ $^1S^e$ TDGI	+1	7.493[3]		
$3s^2$-$3s4s$ $^1S^e$ TDGI	−1	7.184[3]		
$3s^2$-$3s4s$ $^3S^e$		5.409[3]	9.601[5]	2.078[8]
$3s^2$-$3s4s$ $^3S^e$ TDGI		5.686[3]		

tuning the Mg binding energies to experiment.

The ability of the present semiempirical CI calculation to reproduce the low-lying spectrum can be assessed from Table V. The largest discrepancies occur for the $^2P^o$ symmetry and do not exceed 1.5×10^{-4} hartree.

A further test of integrity of the CI calculations comes from the tabulation of oscillator strengths in Table VI. Besides the present calculation, data from three other systematic calculations are included. These are the valence only CI calculations of Moccia and Spizzo [51], the time-dependent gauge-invariant (TDGI) calculations of Merawa *et al.* [43], and finally the very large multiconfiguration Dirac-Fock calculations of Froese-Fischer [52] which include core-valence correlation (the oscillator strengths quoted from this tabulation are *LS* values averaged over the different *J* levels). All the data quoted from these works are derived from transition matrix elements computed using the length form of the multipole operators.

The present oscillator strengths agree with the MCDF to any accuracy of better than 0.025 for all of the transitions listed in the table. The TDGI calculations clearly give oscillator strengths of poorer accuracy than any of the other calculations. The level of approximations made in the TDGI calculation are greater than in the present CI calculation.

The definitions of the scalar and tensor polarizabilities for general states have been given in [26] and do not need to be repeated here. The static dipole and quadrupole polarizabilities are given in Table V. In addition, the tensor part of the polarizability for dipole excitations is also given. The polarizabilities for the $3s^2$ $^1S^e$ could hardly be in any better agreement with the MBPT values of Porsev and Derevianko [42]. The TDGI value for the ground state is about 3% larger than

TABLE VIII. The dispersion coefficients for the $3s^2$-$3snl$ combinations of magnesium. Data by other groups are identified by the citation in the first column. The numbers in the square brackets denote powers of 10.

			$3s3p$ states		
System	β	C_3 (a.u.)	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
$3s^2$-$3s3p$ $^1P^o$ Σ	+1	10.84	2.292[3]	4.161[5]	5.471[7]
TDGI (Ref. [43])	+1		1.797[3]		
$3s^2$-$3s3p$ $^1P^o$ Σ	−1	−10.84	2.292[3]	6.664[5]	9.325[7]
TDGI (Ref. [43])	−1		1.797[3]		
$3s^2$-$3s3p$ $^1P^o$ Π	+1	−5.420	1.395[3]	1.034[5]	6.408[6]
TDGI (Ref. [43])	+1		947		
$3s^2$-$3s3p$ $^1P^o$ Π	−1	5.420	1.395[3]	7.730[4]	3.087[6]
TDGI (Ref. [43])	−1		947		
$3s^2$-$3s3p$ $^3P^o$ Σ			859.7	1.612[5]	1.609[7]
TDGI (Ref. [43])			789		
$3s^2$-$3s3p$ $^3P^o$ Π			753.6	3.646[4]	2.043[6]
TDGI (Ref. [43])			534		
			$3s3d$ states		
System	β	C_5 (a.u.)	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
$3s^2$-$3s3d$ $^1D^e$ Σ	+1	−416.5	4.889[3]	2.357[6]	9.252[8]
$3s^2$-$3s3d$ $^1D^e$ Σ	−1	416.5	4.170[3]	2.140[6]	8.417[8]
$3s^2$-$3s3d$ $^1D^e$ Π	+1	277.7	3.819[3]	7.765[5]	6.388[7]
$3s^2$-$3s3d$ $^1D^e$ Π	−1	−277.7	4.298[3]	8.646[5]	8.487[7]
$3s^2$-$3s3d$ $^1D^e\Delta$	+1	−69.42	2.765[3]	−1.961[4]	5.234[5]
$3s^2$-$3s3d$ $^1D^e$ Δ	−1	69.42	2.525[3]	−2.860[4]	−1.892[6]
$3s^2$-$3s3d$ $^3D^e$ Σ			8.923[3]	4.697[6]	1.924[9]
$3s^2$-$3s3d$ $^3D^e$ Π			7.851[3]	1.605[6]	2.762[8]
$3s^2$-$3s3d$ $^3D^e$ Δ			4.636[3]	−1.168[5]	−3.245[7]

the present value of 71.35. The TDGI dipole polarizabilities are about 5%–10% different from the present set of polarizabilities. The present list of polarizabilities should be regarded as superseding the TDGI values given that the TDGI oscillator strengths and energy differences are less accurate than the present CI values.

B. Dispersion coefficients

The only previous calculation of the dispersion coefficients for the excited states of the Mg dimer was the TDGI method of Merawa *et al.* [43] and here the calculation was limited to only the C_6 parameter. All the dispersion coefficients reported here include core corrections which generally about to a couple of percent.

Table VII gives the dispersion coefficients between the $3s^2$ ground states and excited states of $^1S^e$ and $^3S^e$ symmetries. For the $3s^2$-$3s^2$ interaction the agreement between the present dispersion coefficients and the MBPT values could hardly be better. The two C_6 values are within 0.5%, the C_8 values are within 0.1%, while there is a 1.5% difference for C_{10}. The TDGI calculation gives a value of C_6 that is 7% larger than the present value. The dispersion coefficients for the $3s^2\ ^1S^e$-$3s4s\ ^3S^e$ states were evaluated using the procedures developed for heteronuclear atomic combinations [17]. All dispersion coefficients between states with different spins were evaluated using the heteronuclear program.

Tables VII and VIII list the complete set of dispersion coefficients for the ground state interacting with the $3s3p\ ^1P^o$, $3s3p\ ^3P^o$, $3s3d\ ^1D^e$, $3s3d\ ^3D^e$, $3s4s\ ^1S^e$, and $3s4s\ ^3S^e$ states. Tables IX lists dispersion coefficients connecting the $3s3p\ ^1P^o$ and $3s3p\ ^3P^o$ states.

One noticeable feature from Tables VII and VIII are the differences of up to 40% with the TDGI calculations. The differences most likely result from the limitations in the TDGI description of the underlying atomic structure. The dispersion coefficients with the $^1P^o$ are generally larger than those with the $^3P^o$ levels. This is consistent with the respective sizes of the dipole and quadrupole polarizabilities given in Table V. The relative size of the C_3 and C_6 coefficients for the $3s^2\ ^1S^e$-$3s3p\ ^1P^o$ potentials leads to the C_3/R^3 being larger than the C_6/R^6 term for $R > 6a_0$.

The C_6 dispersion coefficients for the $3s^2$-$3s3p\ ^3P^o$ configuration are not much larger than that of the ground state dimer. The Σ state value of 859.7 a.u. is 30% larger than the ground state value while the Π value is only 20% larger than the ground state value. This has an impact on the photoassociation spectroscopy of the weak transition between the $^1S_0^o$ and $^3P_1^o$ states [60].

Table IX lists the dispersion coefficients between the $3s3p$ configurations. The wave functions for the Σ_1 states change sign upon reflection through a plane containing the two nuclei, while the Σ_2 and Σ_3 states do not change sign. It should be noted that there are off-diagonal terms connecting the two Π states for the dispersion interaction between the $3s3p\ ^1P^o$ and $3s3p\ ^3P^o$ states. However, the off-diagonal terms vanish if the two P states are identical, e.g., the $^1P^o$-$^1P^o$ and $^3P^o$-$^3P^o$ cases.

TABLE IX. The dispersion coefficients for the $3s3p$-$3s3p$ Mg configurations. The Σ_2-Σ_3 row gives the off-diagonal dispersion coefficients between the two states. The Π_1-Π_2 row gives the off-diagonal dispersion coefficients in cases where the off-diagonal terms are nonzero. The numbers in the square brackets denote powers of 10.

System	C_5 (a.u.)	C_6 (a.u.)	C_8 (a.u.)	C_{10} (a.u.)
		$^3P^o$-$^3P^o$ manifold		
Σ_1	0	2.780[3]	8.725[4]	1.082[6]
Σ_2	0	−1.094[3]	8.937[5]	3.180[8]
Σ_3	−1.244[3]	−1.234[4]	1.729[6]	6.004[8]
Σ_2/Σ_3	0	2.229[3]	−9.492[5]	−3.657[8]
Π_1	829.2	3.286[3]	1.009[6]	6.528[7]
Π_2	0	−1.307[3]	1.156[6]	2.939[8]
Δ	−207.3	482.7	1.885[5]	6.083[7]
		$^1P^o$-$^3P^o$ manifold		
Σ_1	0	9.287[3]	4.394[4]	1.641[6]
Σ_2	0	1.312[3]	6.781[5]	7.902[7]
Σ_3	−890.0	1.722[4]	6.803[5]	2.206[8]
Σ_2/Σ_3	0	−28.70	−4.878[5]	−1.486[8]
Π_1	593.4	1.931[4]	4.751[5]	1.586[7]
Π_2	0	3.321[3]	7.907[5]	7.824[7]
Π_1/Π_2	0	5.813[3]	2.567[5]	9.023[6]
Δ	−148.3	1.292[3]	2.221[5]	−1.370[6]
		$^3P^o$-$^3P^o$ manifold		
Σ_1	0	898.4	2.605[4]	8.116[5]
Σ_2	0	1.005[3]	1.407[5]	1.816[7]
Σ_3	−636.9	1.144[3]	2.827[5]	5.153[7]
Σ_2/Σ_3	0	−129.1	−1.592[5]	−2.988[7]
Π_1	424.6	1.016[3]	1.746[5]	7.357[6]
Π_2	0	1.046[3]	1.876[5]	1.796[7]
Δ	−106.1	913.8	3.091[4]	1.270[6]

V. CONCLUSIONS

A systematic approach to the determination of the dispersion parameters for two homonuclear atoms has been developed. The determination of the van der Waals coefficients in the homonuclear case for almost any two lying atomic states has been reduced to a process that is purely mechanical. One simply generates files containing arrays of state and reduced matrix element information, and then feeds them into the dispersion coefficient program. The method has been applied to generate the dispersion coefficients for the lowest molecular states of the sodium and magnesium dimers. The values for sodium generally agree with the model potential values of Marinescu and co-workers [3,10] with the exception of the $3s$-$4p$ and $3p$-$3p$ states. It should be noted that an earlier investigation of homonuclear Li [26] resulted in many discrepancies with the dispersion coefficients of Marinescu *et al.* [3,10] for the more highly excited states. The values for magnesium show differences of up to 40% with the TDGI values of Merawa *et al.* [43]. These differences arise as a result of the approximations inherent in the TDGI approach.

The Feshbach partitioning [16,31] provides guidance about how to handle the cases when both atoms are in states with nonzero angular momentum. For example, the first-order quadrupole interaction defines the molecular representation at long distances in the case of two atoms with $l_a=l_b=1$. As the atoms approach, the off-diagonal terms in the second-order interaction can cause mixing of some of the molecular representations. One can avoid the possibilities of a double excitation to degenerate states in the dispersion interaction by diagonalizing the full first and second interactions at various internuclear distances. The minimum information needed to achieve this is a specification of the diagonal and off-diagonal dispersion coefficients.

At the moment there is very little information available for the long-range interactions of alkaline-earth excited states with other atoms although some information exists for the metastable triplet states [16,61,62]. The present dispersion coefficients could be used to extend existing tables of *ab initio* potential curves [44] to infinite nuclear separation. The only previous dispersion coefficients come from the TDGI calculations of Merawa *et al.* [43,63] for combinations of Mg and Ca atoms. The errors of up to 40% in the TDGI dispersion coefficients for the Mg dimer have obvious implications about the accuracy of their results for the Ca-Mg and Ca-Ca dimers. Generating sets of dispersion coefficients for the other group II and IIB atoms of the periodic table (e.g., Ca or Zn) might be tedious, but it would not be difficult. The major computational task would be simply running the atomic structure programs for all the necessary symmetries, and then assembling the lists of reduced matrix elements into one coherent data file.

Some qualifications are in order. All considerations of electron spin have been omitted from this paper. The assumption has been made that the electron-electron operator does not change the overall spin state of the two atoms. So the van der Waals interactions between two atoms can be calculated without any reference to the spin state. Second, the impact of the spin-orbit interaction has been ignored.

ACKNOWLEDGMENTS

The authors would like to thank S. Caple of CDU for workstation support.

[1] A. Dalgarno and W. D. Davison, Adv. At. Mol. Phys. **2**, 1 (1966).
[2] A. Dalgarno, Adv. Chem. Phys. **12**, 143 (1967).
[3] M. Marinescu, H. R. Sadeghpour, and A. Dalgarno, Phys. Rev. A **49**, 982 (1994).
[4] A. Dervianko, J. F. Babb, and A. Dalgarno, Phys. Rev. A **63**, 052704 (2001).
[5] Z. C. Yan, J. F. Babb, A. Dalgarno, and G. W. F. Drake, Phys. Rev. A **54**, 2824 (1996).
[6] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 052714 (2003).
[7] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 062710 (2003).
[8] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **71**, 019902(E) (2005); **71**, 019903(E) (2005).
[9] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **71**, 042701 (2005).
[10] M. Marinescu and A. Dalgarno, Phys. Rev. A **52**, 311 (1995).
[11] I. Russier-Antoine, A. J. Ross, M. Aubert-Frécon, F. Martin, and P. Crozet, J. Phys. B **33**, 2753 (2000).
[12] M. Marinescu, Phys. Rev. A **56**, 4764 (1997).
[13] B. Bussery and M. A. Frecon, J. Chem. Phys. **82**, 3224 (1985).
[14] B. Bussery and M. A. Frecon, J. Mol. Spectrosc. **115**, 169 (1986).
[15] V. D. Ovsiannikov, Opt. Spectrosc. **53**, 357 (1982).
[16] R. Santra and C. H. Greene, Phys. Rev. A **67**, 062713 (2003).
[17] J. Y. Zhang and J. Mitroy, Phys. Rev. A **76**, 022705 (2007).
[18] J. F. Bukta and W. J. Meath, Mol. Phys. **27**, 1235 (1974).
[19] G. Peach, in *Atoms and Astrophysics*, edited by P. G. Burke, W. B. Eissner, D. G. Hummer, and I. C. Percival (Plenum, New York, 1983), Chap. 5, p. 115.
[20] V. D. Ovsiannikov, A. V. Guilyarovski, and O. Y. Loptako, Mol. Phys. **64**, 111 (1988).
[21] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988).
[22] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **70**, 052503 (2004).
[23] R. R. Whitehead, A. Watt, B. J. Cole, and I. Morrison, Adv. Nucl. Phys. **9**, 123 (1977).
[24] A. Derevianko, W. R. Johnson, M. S. Safronova, and J. F. Babb, Phys. Rev. Lett. **82**, 3589 (1999).
[25] S. G. Porsev and A. Derevianko, J. Chem. Phys. **119**, 844 (2003).
[26] J. Y. Zhang, J. Mitroy, and M. W. J. Bromley, Phys. Rev. A **75**, 042509 (2007).
[27] J. Y. Zhang, Z. C. Yan, D. Vrinceanu, J. F. Babb, and H. R. Sadeghpour, Phys. Rev. A **76**, 012723 (2007).
[28] J. Y. Zhang, Z. C. Yan, D. Vrinceanu, J. F. Babb, and H. R. Sadeghpour, Phys. Rev. A **74**, 014704 (2006).
[29] J. Y. Zhang, Z. C. Yan, D. Vrinceanu, J. F. Babb, and H. R. Sadeghpour, Phys. Rev. A **73**, 022710 (2006).
[30] M. Marinescu and H. R. Sadeghpour, Phys. Rev. A **59**, 390 (1999).
[31] H. Feshbach, Rev. Mod. Phys. **36**, 1076 (1964).
[32] A. Derevianko and A. Dalgarno, Phys. Rev. A **62**, 062501 (2000).
[33] J. Mitroy, D. C. Griffin, D. W. Norcross, and M. S. Pindzola, Phys. Rev. A **38**, 3339 (1988).
[34] J. Mitroy, J. Phys. B **26**, 2201 (1993).
[35] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 062505 (2002).
[36] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 035201 (2003).
[37] J. Mitroy and J. Y. Zhang, Phys. Rev. A **76**, 032706 (2007).
[38] S. Hameed, A. Herzenberg, and M. G. James, J. Phys. B **1**, 822 (1968).
[39] S. Hameed, J. Phys. B **5**, 746 (1972).
[40] C. E. Moore, *Atomic Energy Levels (Molybdenum-Actinium NSRDS-NBS 35)* (US GPO, Washington, DC, 1971), Vol. 3.

[41] Y. Ralchenko, F.-C. Jou, D. Kelleher, A. Kramida, A. Musgrove, J. Reader, W. Wiese, and K. Olsen, NIST Atomic Spectra Database Version 3.1.2, 2007, URL: http://physics.nist.gov/cgi-bin/AtData/main_asd

[42] S. G. Porsev and A. Derevianko, JETP **129**, 227 (2006).

[43] M. Merawa, D. Begue, M. Rerat, and C. Pouchan, Chem. Phys. Lett. **334**, 403 (2001).

[44] E. Czuchaj, M. Krosnicki, and H. Stoll, Theor. Chem. Acc. **107**, 27 (2001).

[45] M. Machholm, P. S. Julienne, and K. A. Suominen, Phys. Rev. A **59**, R4113 (1999).

[46] M. Machholm, P. S. Julienne, and K.-A. Suominen, Phys. Rev. A **64**, 033425 (2001).

[47] K. M. Jones, E. Tiesinga, P. D. Lett, and P. S. Julienne, Rev. Mod. Phys. **78**, 483 (2006).

[48] K. G. Dyall and A. D. McLean, J. Chem. Phys. **97**, 8424 (1992).

[49] F. Tao and Y. Pan, Mol. Phys. **81**, 507 (1994).

[50] E. Tiesinga, S. Kotochigova, and P. S. Julienne, Phys. Rev. A **65**, 042722 (2002).

[51] R. Moccia and P. Spizzo, J. Phys. B **21**, 1121 (1988).

[52] C. Froese Fischer, G. Tachiev, and A. Irimia, At. Data Nucl. Data Tables **92**, 607 (2006).

[53] L. Lundin, B. Engman, J. Hilke, and I. Martinson, Phys. Scr. **8**, 274 (1973).

[54] C. J. Mitchell, J. Phys. B **8**, 25 (1975).

[55] G. Jonsson, S. Kroll, A. Persson, and S. Svanberg, Phys. Rev. A **30**, 2429 (1984).

[56] H. J. Andra, in *Progress in Atomic Spectroscopy, Part B*, edited by W. Hanle and H. Kleinpoppen (Plenum, New York, 1979), Chap. 20, p. 829.

[57] K. Ueda, M. Kawasawa, and K. Fukuda, J. Phys. Soc. Jpn. **51**, 2267 (1982).

[58] M. Aldenius, J. D. Tanner, S. Johansson, H. Lundberg, and S. G. Ryan, Astron. Astrophys. **461**, 767 (2007).

[59] M. Kwiatkowski, U. Teppner, and P. Zimmermann, Z. Phys. A **294**, 109 (1980).

[60] R. Ciurylo, E. Tiesinga, S. Kotochigova, and P. S. Julienne, Phys. Rev. A **70**, 062710 (2004).

[61] R. Santra, K. V. Christ, and C. H. Greene, Phys. Rev. A **69**, 042510 (2004).

[62] A. Derevianko, S. G. Porsev, S. Kotochigova, E. Tiesinga, and P. S. Julienne, Phys. Rev. Lett. **90**, 063002 (2003).

[63] M. Merawa, C. Tendero, and M. Rerat, Chem. Phys. Lett. **343**, 397 (2001).