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Effective Hamiltonian for atomic collective spectra

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A simple effective energy operator is constructed for doubly excited two-electron atoms. This operator generalizes the ‘‘molecular’’ Hamiltonian of the supermultiplet model based in approximate $O(4)$ symmetry. The Hamiltonian is compared to spectra of two-electron systems with both electrons in the $n=2$ shell. Nonlinear least-squares fits show systematic trends related to shielding, independent particle, and correlation effects. Operators for atoms with three or more outer electrons are briefly considered.
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I. INTRODUCTION

Investigations of highly excited few-body systems are bringing to light many surprising developments, in problems as disparate as the motion of electrons in atoms, and the vibrational dynamics of molecules. The idea that doubly excited states of atoms exhibit moleculelike collective motions has proven very fruitful for understanding electron correlation [1–23].

However, it is unlikely that the small-amplitude rovibrational model can provide an adequate metaphor for the entirety of correlated behavior in highly excited atoms. The two-electron ‘‘molecular’’ model is based in approximate $O(4)$ symmetry. There are indications [24,25] that the constants of motion of this symmetry are broken, especially for systems with two electrons outside a closed shell. Furthermore, there are large systematic differences in the spectral patterns of two-electron atoms and systems with two electrons outside a closed shell, with both deviating from the ideal ‘‘molecular’’ Hamiltonian obtained from $O(4)$ algebra.

Nonetheless, atoms with closed inner shells still seem to be governed by collective motion [6,9,10], perhaps in some more general picture. Like doubly excited helium [5], systems with closed shells display [9] correlation in their ground and singly excited states, and in doubly excited states with the electrons in different shells. Extensive analysis of two-electron wave functions [9,10] of systems with and without closed shells have confirmed the basic validity of the heuristic picture of a highly nonrigid system with bending excitations.

In addition, there are surprising new phenomena in two-electron systems not predicted by the $O(4)$ model, such as the ‘‘frozen planet states’’ [20], where the linear ‘‘molecular’’ atom ‘‘isomerizes’’ and the electrons become locked into place on the same side of the nucleus. In the frozen planet systems, there are even hints [8,14–16] of nonlinear resonance phenomena between collective modes, analogous to Fermi resonances long familiar in molecules. Finally, for mathematical reasons discussed below, there are perhaps intractable problems with extending a symmetry-based ‘‘molecular’’ picture to atoms with three or more electrons. Nonetheless, evidence is starting to appear [26–28] for moleculelike collective effects in systems with three outer electrons. Again, the spectral patterns differ substantially for systems with [27,28] and without [29] closed shells.

In short, the concepts and symbols available from the $O(4)$ symmetry model are too limited to encompass the full range and subtlety of complex behavior emerging in highly excited atoms. This paper begins exploration of an approach using effective energy correlation operators. The essential starting point is approximate dynamical symmetry, but our goal necessarily will take us beyond the realm of symmetry.

It is expected that the effective energy operators will be useful for interpreting patterns that are not well represented by either the idealized independent particle or collective limits. The applications presented here are numerical tests for $n=2$ states of the doubly excited He and Be isoelectronic series. Even for systems seemingly as simple as these, there are critical puzzles in the known spectral patterns. The effective energy operator tested here brings considerable light to bear on this. Open questions are whether this approach will be useful for higher shells and for atoms with three or more electrons.

II. $O(4)$ EFFECTIVE HAMILTONIAN AND THE ROTOR-VIBRATOR SUPERMULTIPLET SCHEME

Around 1980, a new classification scheme and physical model were developed for doubly excited states of two-electron atoms. States were grouped into ‘‘supermultiplets’’ that could be interpreted in terms of collective rotation-vibration modes of a correlated, but highly nonrigid linear ‘‘molecular’’ structure for the atom [1–7].

The supermultiplet scheme grew out of earlier work [30–32] in which the total angular momentum

$$\vec{L}=\vec{l}_1+\vec{l}_2 \tag{1}$$

was combined with the difference of the Runge-Lenz operators

$$\vec{B}=\vec{a}_1-\vec{a}_2 \tag{2}$$

to form an approximate symmetry group $O(4)_{12}$ for the atom. Previously, the more obvious choice

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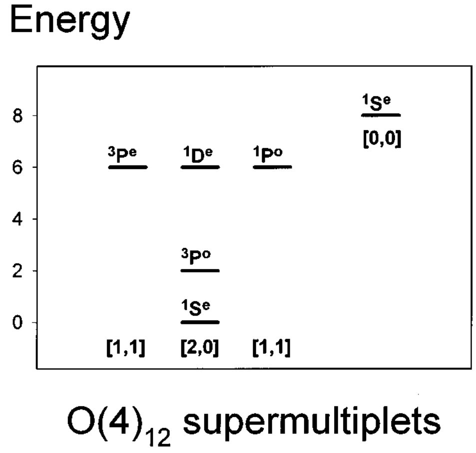

FIG. 1. Supermultiplets for both electrons in the $n=2$ shell. Each column is an $O(4)_{12}$ multiplet, labeled by quantum numbers $[P,T]$. Each level is an atomic term labeled $^{2S+1}L^{\pi}$.

$$\vec{A}=\vec{a}_1+\vec{a}_2 \tag{3}$$

had been found [33,34] not to work, following work [35,36] suggesting a ''physical'' $O(4)$ that hinted at the existence of the symmetry group eventually identified as $O(4)_{12}$. The idea behind using the difference $\vec{B}=\vec{a}_1-\vec{a}_2$ was that it mimics the Coulomb repulsion between the electrons, whether in the same or disparate shells [30–32,37].

From the $O(4)_{12}$ quantum numbers P,T is formed [38] the invariant operator $[P(P+2)+T^2]$. This can be regarded as the first piece, see Eq. (4), of the simplest version of an $O(4)_{12}$ effective energy operator for the atom [7]. The eigenvalues of this operator can be grouped into ''supermultiplets'' with the energy and $^{2S+1}L^{\pi}$ quantum number pattern of a linear XYX ''molecular'' rotor vibrator with the electrons X on opposite sides of the nucleus, and fermion statistics. This ''molecular'' spectrum is shown for $n=2$ in Fig. 1.

III. GENERALIZED EFFECTIVE ENERGY OPERATOR FOR TWO-ELECTRON CORRELATION

The Hamiltonian based on the algebra $O(4)_{12}$ has given a reasonable ideal model for doubly excited two-electron atoms as a ''molecular'' rotor-vibrator system. I will use this as the point of departure to devise effective Hamiltonians more general than the ideal case.

A. Spectral patterns in He and Be isoelectronic series

The spectral systems to be considered are of two kinds: He and isoelectronic ions doubly excited to the $n=2$ shell; and Be and its isoelectronic series, with two electrons outside a closed $1s^2$ shell. With both electrons in $n=2$, there are six allowed terms. The He and Be spectra are plotted as supermultiplets in Figs. 2(a) and 5(a). Both spectra agree qualitatively with the rotor-vibrator model, as noted in Ref. [6]. However, significant differences between the spectral patterns of the two atoms are evident. The most notable difference is the sign of the splitting between the pair of levels $^1P^o$ and $^3P^e$, each of which has one bending quantum. In molecules, these are split due to rotation-vibration interaction [39], and the splitting is known as l doubling. A similar splitting occurs in the rotational spectrum of a slightly asymmetric rotor, but with opposite sign. In He the splitting has the opposite sign of molecular l doubling. This splitting increases with Z along the isoelectronic series, as seen in Fig.

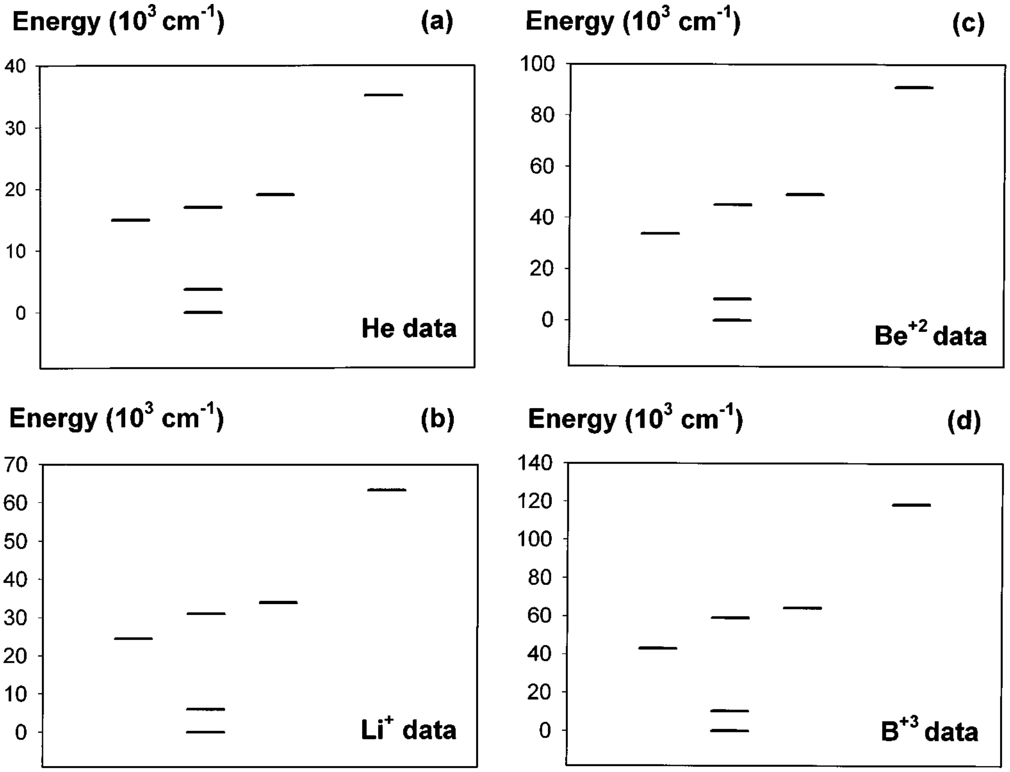

FIG. 2. Calculated data for $n=2$ levels of He isoelectronic series, from Ref. [46], with energies converted to cm^{-1}.

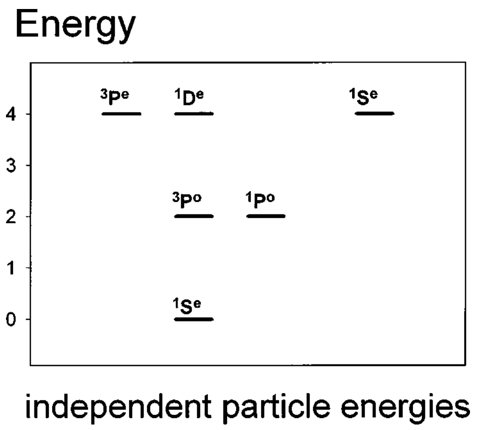

FIG. 3. Energy levels of supermultiplets with just the single-particle terms $\vec{a}_i^2$ contributing to H^{eff}.

2. In Be the splitting has the same sign as the molecular l doubling, and in this respect, as in others [6], the Be spectrum is more like that of a linear symmetric top molecule than is the He spectrum.

In the ideal $O(4)_{12}$ limit, there is no splitting between the $^1P^o$ and $^3P^e$, as seen in Fig. 1. Can the existence of the splitting in real atoms, and the prominent difference in the spectral pattern of Be and He, be accounted for with an effective Hamiltonian operator? For this, an effective Hamiltonian must be constructed that goes beyond the ideal $O(4)_{12}$ limit.

B. Single-particle and correlation operators

The effective Hamiltonian will have ‘‘single-particle’’ and ‘‘correlation’’ contributions, of variable relative strength. In this way, one can think of an effective Hamiltonian intermediate between single-particle and correlation limits.

To develop this, I examine relevant pieces of the energy operator of Ref. [7], the $O(4)_{12}$ and $O(3)_{12}$ parts, expressed in terms of the angular momentum and Runge-Lenz operators,

$$\begin{aligned} &B[P(P+2)+T^2]+CL(L+1)\\ &\quad=B[L(L+1)+(\vec{a}_1-\vec{a}_2)^2]+CL(L+1)\\ &\quad=B(\vec{a}_1-\vec{a}_2)^2+\gamma L(L+1)\\ &\quad=B(\vec{a}_1^2+\vec{a}_2^2-2\vec{a}_1\cdot\vec{a}_2)+\gamma L(L+1). \end{aligned} \tag{4}$$

The final expression shows that the effective energy consists of single-electron terms proportional to $\vec{a}_i^2$, a two-electron ‘‘correlation term’’ $\vec{a}_1\cdot\vec{a}_2$, and an angular momentum term $\gamma L(L+1)$ to take into account the effective moment of inertia of the rotor. The terms $\vec{a}_i^2$ can be thought of as effective single-electron contributions to the energy. Empirically, they enter with a negative value of B in Eq. (4). This is important, because it corresponds, e.g., for the $n=2$ manifold, to the ordering $2s<2p$ of single-particle orbital energies. The $2s$-$2p$ splitting originates as a mean-field effect from electron shielding, and the $\vec{a}_i^2$ single-particle contributions can be taken to represent this. Figure 3 shows the supermultiplet spectrum with just the single-particle contributions. If it can be said at all that the single-particle contributions $\vec{a}_i^2$ give the embryonic form of the supermultiplet energy pattern of Fig. 1, it is evident the correlation term $\vec{a}_1\cdot\vec{a}_2$ is needed to ‘‘crystallize’’ the rotor-vibrator pattern.

The single-particle ordering $2s<2p$ means that a correlation term $\vec{a}_1\cdot\vec{a}_2$ with sign opposite that of $\vec{a}_i^2$, as with $(\vec{a}_1-\vec{a}_2)^2$ in $O(4)_{12}$, makes a positive contribution to the energy, and so corresponds to a repulsive interaction. This is just what we want in the effective energy operator: single-particle states with $2s<2p$ correlated by repulsive interaction to give a ‘‘molecular’’ structure whose lowest state has the electrons on opposite sides of the nucleus, with higher states described as collective excitations of the linear structure.

C. A generalized effective energy operator

In the effective $O(4)_{12}$ rotor-vibrator operator Eq. (4), the single-particle and correlation terms enter with equal magnitude B. A simple generalization is to let the single-particle and correlation terms enter with different strengths α and α_{12},

$$H^{\text{eff}}=\alpha(\vec{a}_1^2+\vec{a}_2^2)-2\alpha_{12}\vec{a}_1\cdot\vec{a}_2+\gamma L(L+1). \tag{5}$$

The effective energy operator, therefore, has variable single-particle and correlation contributions. An operator with variable α_{12} has been considered before in the context of models for configuration mixing [40] and quasiclassical models [41,42] for $L=0$ states.

It is important to recognize that the operator H^{eff} is by no means the only way to introduce variable single-particle and correlation contributions. H^{eff} is obtained by breaking an $O(4)_{12}$ algebra that can itself be obtained [7] from a $U(4)_{12}$ algebra in the chain

$$U(4)_1\times U(4)_2\supset U(4)_{12}\supset O(4)_{12}\supset O(3)_{12}. \tag{6}$$

However, an alternate chain [43] is

$$U(4)_1\times U(4)_2\supset U(4)_{12}\supset U(3)_{12}\supset O(3)_{12}, \tag{7}$$

where the $U(3)_{12}$ corresponds to nonrigid systems without correlation. The chains (6) and (7) are related to different patterns of ideal ‘‘rigid and nonrigid limit’’ few-body spectra [44,45]. It would be entirely reasonable to obtain a single-particle contribution from breaking of the operators in the second, nonrigid limit chain (7) and then combine this with elements from the rigid molecule chain (6) to get the overall H^{eff}. This would make no difference whatsoever from Eq. (5) in the present investigation of the $n=2$ shell, but would matter for higher shells. The kinds of effective energy operators that are best will, in all likelihood, be determined from experience with a variety of problems of increasing complexity.

To test the operator H^{eff} of Eq. (5), I performed nonlinear least-squares fits on calculated spectra [46] for the isoelectronic series He, Li^+, Be^{2+}, Be^{3+}, up-to-date experimental levels [47] for neutral Be, and somewhat questionable but still illuminating (see below) compilations of Moore [48] for the Be isoelectronic ions. All energies were converted to cm^{-1}. Several fits were done with variation of different combinations of the parameters in H^{eff}. The energy of the

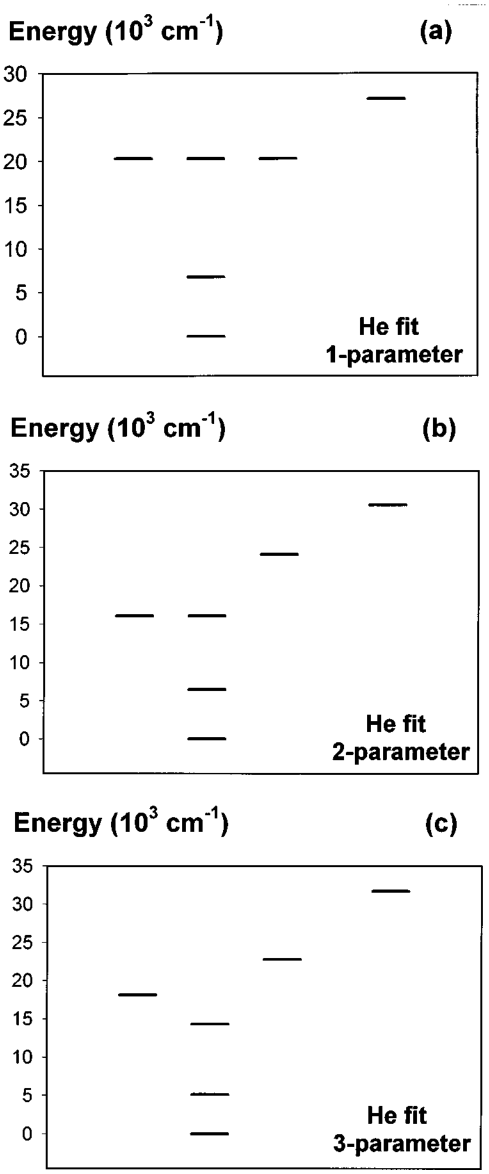

FIG. 4. Fits of the He spectrum of Fig. 2(a) to several versions of H^{eff}. (a) One-parameter fit with $\alpha=\alpha_{12}$ and $\gamma=0$; (b) two-parameter fit with variable α, α_{12}; (c) three-parameter fit with variable α, α_{12}, γ. See Sec. III C for discussion.

lowest $^1S^e$ level with $n=2$ for each atom was set equal to the energy of the lowest $^1S^e$ level in the fit. Each fit is then of five independent levels.

D. Results of the fits

1. He isoelectronic series

We begin with several fits for He. The first was a one-parameter fit with $\alpha=\alpha_{12}$ and $\gamma=0$. These are the ideal $O(4)_{12}$ supermultiplets, and the results in Fig. 4(a), of course, have the spectral pattern of Fig. 1.

A deficiency of this fit is that there is no *l*-type splitting between the one-quantum bend states $^1P^o$ and $^3P^e$. This can be remedied by allowing variation of the parameter α_{12} for the correlation term $\vec{a}_1\cdot\vec{a}_2$, along with α. The results are shown in Fig. 4(b) and Table I. Figure 4(b) shows that the correct sign and approximate magnitude of the $^1P^o$-$^3P^e$ splitting are obtained. Note that the signs of α and α_{12} in Table I mean that the single-particle and correlation terms enter with opposite signs in the fit to H^{eff}, Eq. (5). It is reassuring that the fit works like this numerically, given the expectation on theoretical grounds that it must be this way. A slight further improvement, shown in Fig. 4(c), is obtained by allowing a variation of γ, as in Eq. (5). There is still a minor but annoying discrepancy of the position of the higher rotor state, $^1D^e$. A better ‘‘eyeball’’ fit can be obtained by changing the parameter γ [see above, immediately following Eq. (4)], but this results in a worse *rms* deviation, and is not shown.

The spectra for the four isoelectronic two-electron atoms He, Li^+, Be^{2+}, B^{3+}, in Fig. 2, are very similar, as are their fits, which are reported in Table I, but not shown pictorially. As noted above, the most significant trend along the series is the increasing relative magnitude of the $^1P^o$-$^3P^e$ splitting.

The trends in the sign and magnitude of the splitting can be related to the parameters of the fits, which show meaningful trends, with simple interpretations using concepts of atomic and molecular theory. Recall that the substantial deviation from the ideal $O(4)_{12}$ supermultiplets of Fig. 1 comes about in the molecular model because of the sign and magnitude of the *l*-type doubling. In the fits of the isoelectronic two-electron series, the salient trend is that the ratio α/α_{12} is less than 1.0 and decreases with nuclear charge Z. With respect to H^{eff}, this means increasing importance with Z of the correlation term $\vec{a}_1\cdot\vec{a}_2$, compared to the single-particle terms $\vec{a}_i^2$. (At first glance, this seems in conflict with the expectation that the interelectronic repulsion becomes less important with increasing Z. However, the energy operator is intended to account only for the pattern *among* the six levels in the $n=2$ shell, not the *overall energy* of the $n=2$ manifold. The latter is indeed controlled by Z.) This dominance of the correlation $\vec{a}_1\cdot\vec{a}_2$ is understood by recalling that the single-particle terms $\alpha\vec{a}_i^2$ describe the $2s$-$2p$ splitting, which is due to shielding. Because the shielding of each electron is only by the other electron in the $n=2$ shell, it is expected to be much smaller than shielding by a closed inner shell. This is favorable for our interpretation, because the $2s$-$2p$ shielding splitting contributes to the $^1P^o$-$^3P^e$ splitting with the *wrong* sign for He, as seen in the ‘‘single-particle supermultiplets’’ shown in Fig. 3, as opposed to the $^1P^o$-$^3P^e$ splitting contribution from the correlation

TABLE I. Parameters from fits of the effective energy operator H^{eff} to atomic data. The different fits are described in Sec. III C.

	He	He	He	Li^+	Be^{2+}	B^{3+}	Be	Be	B^+	C^{2+}	N^{3+}
$-\alpha\,(\times 10^3\ \mathrm{cm}^{-1})$	3.383 00	0.394 19	2.076 98	2.550 96	2.830 35	3.063 10	1.283 39	1.537 67	2.471 42	3.487 84	4.483 07
$-\alpha_{12}$	3.383 00	4.405 46	4.416 05	8.000 75	11.546 29	15.049 51	0.669 87	0.577 19	1.023 39	1.453 34	1.861 18
$-\gamma$			0.947 02	1.332 04	1.614 57	1.866 60		0.200 92	0.191 46	0.273 01	0.338 78
α/α_{12}	1.000 0	0.089 47	0.470 3	0.318 8	0.245 1	0.203 5	1.915 9	2.664 1	2.414 9	2.399 9	2.408 7

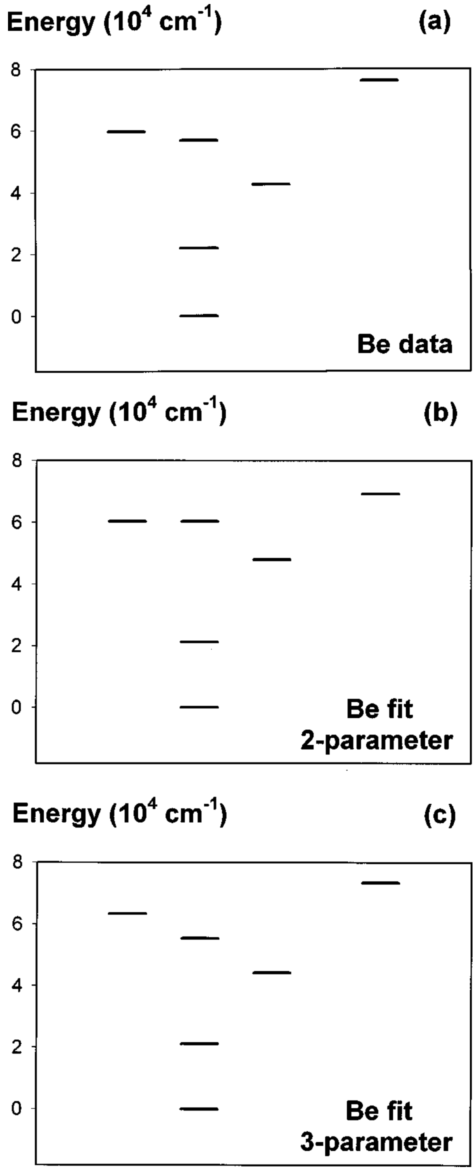

FIG. 5. (a) Data for $n=2$ levels of Be from Ref. [47]; (b) two-parameter fit of data to H^{eff} with variable α α_{12}; (c) three-parameter fit with variable α, α_{12}, γ. See Sec. III C for discussion.

$\alpha_{12}\vec{a}_1\cdot\vec{a}_2$, which enters with the correct sign. Furthermore, shielding is expected to decrease with Z relative to the correlation term, consistent with the observed trend of increasing splitting magnitude along the He series. To summarize: the small and decreasing ratio α/α_{12} is responsible for the sign and magnitude of the ${}^1P^o$-${}^3P^e$ splitting along the series in Fig. 2, and relates them to the basic notions of shielding and correlation in a consistent fashion.

2. Be isoelectronic series

Now for the spectra and fits of the Be isoelectronic series. The results for Be are shown in Fig. 5; the results for the rest of the series are reported in Table I but not shown pictorially. Visually, the agreement with the data is good for Be, and better than for the He isoelectronic series. The data for Be are taken from the up-to-date compilation of Kramida and Martin [47]. This differs from the older compilation of Moore [48] primarily in a small difference in the ${}^1D^e$ level and a considerable difference in the upper ${}^1S^e$ level; the crucial ${}^1P^o$-${}^3P^e$ splitting is essentially unaffected. For the Be isoelectronic ions, an up-to-date compilation does not appear to be available. I went ahead and used the assignments and levels of Moore for fits of the ions, because for neutral Be, the fits of the Kramida-Martin and Moore data do not differ all that much, especially in regard to the ${}^1P^o$-${}^3P^e$ splitting.

The most notable trend along the Be isoelectronic series is the reversal in sign of the ${}^1P^o$-${}^3P^e$ splitting in comparison with the He series. This trend can again be interpreted in relation to the fits, given in Table I. For the Be isoelectronic series, the ratio α/α_{12} is now much greater than 1.0. This large α value is responsible for the sign reversal of the ${}^1P^o$-${}^3P^e$ splitting. This corresponds to the greater relative importance of the single-particle terms, which is related in turn to the increased shielding and $2s$-$2p$ splitting expected in an atom with filled $1s^2$ core. It is noteworthy that unlike the He series, the ratio α/α_{12} is approximately constant, consistent with the shielding by the $1s^2$ core being more stable than the shielding in the coreless He series.

It is illuminating to compare the results of these fits with other work that contrasts He-like and Be-like systems. It has long been recognized [6,10,49,50] that there are isomorphic features in the spectra of two-electron systems with and without a closed shell. As we have seen, both Be and He deviate substantially from the ideal $O(4)_{12}$ molecular model, Be with extra single-particle contribution, and He with extra correlation. This is entirely consistent with the conclusion of Martin *et al.* [25] that ‘‘Be-like wave functions have a stronger single $Nlnl'$ configuration character than the two-electron ones.’’ This does not contradict the fact that the sign of the ${}^1P^o$-${}^3P^e$ splitting in Be is more consistent than in He with molecular l doubling; on the contrary, we have seen in the operator H^{eff} that the greater single-configuration character is the source and prerequisite of this. All of this is consistent with the earlier conclusion that the pattern of energy spacings [6] and wave functions [10] is more like a molecular rotor vibrator in Be than in He.

Apparently, the filled core stabilizes the moleculelike structure, and in this sense, plays a role analogous to the central atom in a real triatomic molecule. The core could do this by helping the outer electrons avoid each other, so that they correlate better spatially. Another perspective on this is that the filled core makes the electrons in Be behave more like particles on concentric spheres [11], a model used to elucidate the ‘‘molecular’’ atom. A hollow doubly excited He atom does not do this, so perhaps the correlation contribution in H^{eff} must be greater to keep the electrons away from each other. If the core in Be does make the atomic bending more moleculelike, an interesting question is how the core affects the collective radial quantum number considered by Rost and co-workers [18,19] for He.

E. Higher shells

The preceding considerations have led to a consistent picture of spectral patterns and their physical interpretation for systems with two electrons in the $n=2$ shell. It is of interest whether this picture holds for higher shells.

Calculations of two-electron systems for $n=3$ without closed shell agree completely [4] with the qualitative pattern found here for $n=2$. Calculations [24,51] for closed-shell systems for $n=3$ agree in the main with the patterns found here for $n=2$. The calculations of Ref. [24] for O^{2+} with $n=3$, see, e.g., their Fig. 2, show the level $^3F^e$ slightly lower in energy than $^1F^o$, a reversal from the l-doubling pattern pointed out in the present paper for $n=2$ with closed shell. The calculations of Ref. [24] have been called into question [51–53], but the compilation in Table V of Ref. [51] does seem to support the existence of this switch for the $^3F^e$ and $^1F^o$, and also for a high $^3P^e$ and $^1P^o$ l-doubled pair. Unfortunately, in the various calculations, the relevant levels jump around a fair bit, and any conclusions about the actual energy patterns and their interpretation must remain tentative for the time being. It is entirely plausible, but remains to be demonstrated, that these reversals for states in higher subshells could be accounted for in terms of a modified relation of correlation and independent particle effects, for example, taking a single-particle operator from a chain like Eq. (7) rather than Eq. (6).

IV. ON THE LOSS OF SYMMETRY

The effective Hamiltonian has been tailored to represent systems with varying magnitude of single-particle and correlation contributions by variation of the parameters α, α_{12}, and γ. There is considerable deviation from the ideal $O(4)_{12}$ ‘‘molecular’’ limit, with correlation of greater importance in He and single-particle shielding contributions of greater importance in Be. The variability of these effects is needed to capture the essential spectral patterns and trends along the isoelectronic series.

The penalty for this flexibility is that the Hamiltonian can no longer be expressed in terms of operators from the $O(4)_{12}$ symmetry group. This means that the precise quantum numbers provided by the symmetry classification are no longer available. This is a considerable price, because the symmetry constants are useful to identify quantum numbers for collective modes, as in the original supermultiplet classification [2,3]. The payoff is that sacrifice of the symmetry classification enables a better fit to the data, with significant trends newly interpretable in simple physical terms. However, the most significant implications of the departure from symmetry concern atoms with three or more outer electrons, as I now discuss.

V. ATOMS WITH MORE THAN TWO OUTER ELECTRONS

For three or more electrons, useful generalization of the $O(4)_{12}$ with minus sign in $(\vec{a}_1-\vec{a}_2)$ to a many-particle $O(4)$, if not altogether impossible, has so far eluded accomplishment. This appears to foreclose a group-theoretical treatment analogous to $O(4)_{12}$ of ‘‘molecular’’ atoms with more than two outer electrons, since the repulsive interaction of electrons is the origin of the minus sign for two-electron systems. This is unfortunate, because there is no evident reason why models with molecular quantum numbers should not apply to larger systems, for example, a planar D_{3h} structure for three electrons. Indeed, evidence is starting to appear [26–28] for collective effects in three-electron systems.

In these systems where a symmetry classification may not be feasible at all, renunciation of the symmetry quantum numbers therefore appears not so much as a sacrifice, but rather as the precondition for further progress. Herrick and Kellman [40] investigated an operator Λ to model configuration mixing for multielectron systems. For two electrons, the $O(4)_{12}$ operator $(\vec{a}_1^2+\vec{a}_2^2-2\vec{a}_1\cdot\vec{a}_2)$ is the simplest form of Λ, which was generalized in Ref. [40] to a form similar to the effective energy operators used in the fits here. (See also, Refs. [41,42] for application to quasiclassical treatment of $L=0$ states.) For three or more electrons, it is no longer possible to construct Λ starting with an $O(4)$ operator, but Λ nonetheless gives good predictions of configuration mixing. It is, therefore, reasonable to use the Λ operator as a starting point for building effective energy operators for many-electron systems.

We have seen that an effective energy operator, incorporating effects of shielding and correlation in a very simple way, gives qualitative understanding of spectral patterns of atoms with two electrons in the $n=2$ shell. This involves significant departures, not only from independent particle behavior, but also from the idealized $O(4)$ ‘‘molecular’’ model. Subjects for further investigation of effective energy operators are spectral patterns of higher shells of two-electron systems, including those with filled cores, and three-electron systems with [26–28] and without [29] filled cores, where the spectral patterns differ greatly and the applicability of a molecular model is an open question.

ACKNOWLEDGMENT

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[1] M. E. Kellman and D. R. Herrick, J. Phys. B **11**, L755 (1978).
[2] D. R. Herrick and M. E. Kellman, Phys. Rev. A **21**, 418 (1980).
[3] M. E. Kellman and D. R. Herrick, Phys. Rev. A **22**, 1536 (1980).
[4] D. R. Herrick, M. E. Kellman, and R. D. Poliak, Phys. Rev. A **22**, 1517 (1980).
[5] D. R. Herrick, Adv. Chem. Phys. **52**, 1 (1983).
[6] M. E. Kellman, Phys. Rev. Lett. **55**, 1738 (1985).
[7] M. E. Kellman, Phys. Rev. Lett. **73**, 2543 (1994).
[8] M. E. Kellman, Int. J. Quantum Chem. **65**, 399 (1997).
[9] J. L. Krause and R. S. Berry, Phys. Rev. A **31**, 3502 (1985); J. Chem. Phys. **83**, 5153 (1985).
[10] J. E. Hunter III and R. S. Berry, Phys. Rev. A **36**, 3042 (1987).
[11] G. S. Ezra and R. S. Berry, Phys. Rev. A **28**, 1989 (1983); P. C. Ojha and R. S. Berry, *ibid.* **36**, 1575 (1987).
[12] S. I. Nikitin and V. N. Ostrovsky, J. Phys. B **18**, 4371 (1985).
[13] S. I. Nikitin and V. N. Ostrovsky, J. Phys. B **18**, 4349 (1985).
[14] V. N. Ostrovsky and N. V. Prudov, Phys. Rev. A **51**, 1936 (1995).

[15] V. N. Ostrovsky and N. V. Prudov, J. Phys. B **30**, 151 (1997).
[16] N. V. Prudov and V. N. Ostrovsky, Phys. Rev. Lett. **81**, 285 (1998).
[17] C. D. Lin, Phys. Rev. A **29**, 1019 (1984).
[18] J. M. Rost, R. Gersbacher, K. Richter, J. S. Briggs, and D. Wintgen, J. Phys. B **24**, 2455 (1991).
[19] J. M. Rost and J. S. Briggs, J. Phys. B **24**, 4293 (1991).
[20] K. Richter, J. S. Briggs, D. Wintgen, and E. A. Solov'ev, J. Phys. B **25**, 3929 (1992).
[21] Y. K. Ho, Phys. Scr. **50**, 654 (1994); Phys. Rev. A **50**, 4877 (1994).
[22] J. Muller and J. Burgdorfer, Phys. Rev. Lett. **70**, 2375 (1993).
[23] P. V. Grujic and N. S. Simonovic, J. Phys. B **28**, 1159 (1995).
[24] Z. Chen and C. D. Lin, J. Phys. B **22**, 2875 (1989).
[25] F. Martin, H. Bachau, P. Galan, A. Riera, and M. Yanez, J. Chem. Phys. **94**, 5011 (1991).
[26] V. I. Matveev, Zh. Eksp. Teor. Fiz. **89**, 411 (1985) [Sov. Phys. JETP **62**, 233 (1985)].
[27] S. Watanabe and C. D. Lin, Phys. Rev. A **36**, 511 (1987).
[28] C. G. Bao, X. Yang, and C. D. Lin, Phys. Rev. A **55**, 4168 (1997).
[29] B. C. Gou and K. T. Chung, J. Phys. B **29**, 6103 (1996).
[30] C. E. Wulfman, Chem. Phys. Lett. **23**, 370 (1973).
[31] D. R. Herrick and O. Sinanoglu, J. Chem. Phys. **62**, 886 (1975).
[32] D. R. Herrick and O. Sinanoglu, Phys. Rev. A **11**, 97 (1975).
[33] A. R. P. Rau, Phys. Rev. A **2**, 1600 (1970).
[34] E. Chacon, M. Moshinsky, O. Novaro, and C. E. Wulfman, Phys. Rev. A **3**, 166 (1971).
[35] J. S. Alper and O. Sinanoglu, Phys. Rev. **177**, 77 (1969).
[36] J. S. Alper, Phys. Rev. A **2**, 1603 (1970).
[37] S. I. Nikitin and V. N. Ostrovsky, J. Phys. B **18**, 3141 (1976).
[38] B. G. Wybourne, *Classical Groups for Physicists* (Wiley, New York, 1974).
[39] G. Herzberg, *Infrared and Raman Spectra* (Van Nostrand, New York, 1950).
[40] D. R. Herrick and M. E. Kellman, Phys. Rev. A **18**, 1770 (1978).
[41] S. I. Nikitin and V. N. Ostrovsky, Fiz. Mol. (Kiev) **8**, 3 (1980).
[42] E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **89**, 1991 (1985) [Sov. Phys. JETP **62**, 1148 (1985)].
[43] F. Iachello and R. D. Levine, *Algebraic Theory of Molecules* (Oxford University Press, New York, 1994).
[44] M. E. Kellman, F. Amar, and R. S. Berry, J. Chem. Phys. **73**, 2387 (1980).
[45] M. E. Kellman, Chem. Phys. **48**, 89 (1980).
[46] L. Lipsky, R. Anania, and M. J. Conneely, At. Data Nucl. Data Tables **20**, 127 (1977).
[47] A. Kramida and W. C. Martin, J. Phys. Chem. Ref. Data **26**, 1185 (1997).
[48] C. E. Moore, *Atomic Energy Levels*, Nat'l. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949).
[49] C. H. Greene, Phys. Rev. A **23**, 661 (1981).
[50] P. F. Mahony and C. H. Greene, Phys. Rev. A **31**, 2501 (1985).
[51] M. S. Safranova, U. I. Safranova, N. Nakamura, and S. Ohtani, Phys. Scr. **53**, 689 (1996).
[52] H. Bachau, P. Galan, F. Martin, A. Riera, and M. Yanez, J. Phys. B **23**, L83 (1990).
[53] Z. Chen and C. D. Lin, J. Phys. B **23**, L87 (1990).