

General-model-space many-body perturbation theory: The $(2s\ 3p)^{1,3}P$ states in the Be isoelectronic sequence

Gabriel Hose* and Uzi Kaldor

Chemistry Department, Tel-Aviv University, Tel-Aviv 69978, Israel

(Received 29 May 1984)

The energies of the $(2s\ 3p)^{1,3}P$ states of the Be sequence ions N IV—Ne VII are calculated, with use of a general-model-space many-body perturbation theory (MBPT) to third order. The triplet states are described accurately by a one-configuration model (P) space including only $2s\ 3p$, but the singlets are not; the singlet-triplet separation has the right sign (singlet below triplet) but is only 30% of experiment. Incorporation of the $2p\ 3s$ configuration in the model space greatly improves the results. This incomplete, two-configuration model space yields virtually the same energies as the larger, complete model space required by other quasidegenerate MBPT methods, at one-fifth the computational cost.

I. INTRODUCTION

The $1s^2 2s\ 3p$ states of the Be isoelectronic sequence have been the subject of several recent experimental^{1,2} and theoretical³⁻⁹ investigations. The interesting aspects of the system include an order reversal of the levels, the singlet being lower than the triplet from C III onward, as well as an appreciable moment of the intercombination line $(2s^2)^1S_0 - (2s\ 3p)^3P_1$, making the 3P_1 level much shorter lived than 3P_2 and 3P_0 . Recent calculations, using configuration-interaction (CI) (Refs. 5-7) or multiconfiguration Hartree-Fock (MCHF) (Ref. 9) methods, agree well with experimental energies and lifetimes, so that the system is well understood. It provides a stringent test for a method aimed at calculating correlation energies in atoms and molecules, as the singlet-triplet reversal is an energetically small effect which does not occur at the Hartree-Fock level and is solely due to electron correlation.

The Be sequence $2s\ 3p$ system is used here as a test case for a recently developed¹⁰⁻¹⁴ quasidegenerate many-body perturbation theory (MBPT). The main aspect of the theory to be tested is the partitioning of the determinant Hilbert space and the selection of a model (or P) space, within which an effective Hamiltonian is calculated and diagonalized. Nonrelativistic calculations are carried out for the N IV—Ne VII ions. Relativistic corrections are not very large for these ions; they have been shown⁹ to decrease the singlet-triplet splitting by 4% for O V and 7% for Ne VII.

II. METHOD

Multireference or quasidegenerate MBPT involves the partitioning of the determinant Hilbert space into a d -dimensional model space P and its complement Q , using the projectors

$$P = \sum_{i=1}^d |\Phi_i\rangle\langle\Phi_i|, \quad Q = 1 - P = \sum_{i>d} |\Phi_i\rangle\langle\Phi_i|. \quad (1)$$

A subset of the eigenvalues and eigenfunctions of the Schrödinger equation

$$H\Psi = E\Psi \quad (2)$$

is approximated by diagonalizing an effective Hamiltonian in the model space,

$$H_{\text{eff}}P\Psi = EP\Psi. \quad (3)$$

Multireference MBPT was discussed by Bloch and Horowitz¹⁵ and by Morita,¹⁶ and a fully linked formalism was first derived by Brandow.¹⁷ Brandow's method, or modifications thereof, have been successfully applied to nuclear,¹⁸ atomic,¹⁹ and molecular²⁰ systems.

Brandow's theory,¹⁷ as well as later schemes²¹ for the order-by-order construction of the effective Hamiltonian matrix, require the model space to be complete, i.e., include determinants corresponding to all possible (symmetry-allowed) combinations of open-shell orbitals. The Be sequence $2s\ 3p$ configuration discussed in the present work is known to be close in energy to and interact strongly with the $2p\ 3s$, and the two configurations (four determinants) would be a natural choice for the model space. Completeness requires, however, the inclusion of the $2s\ 2p$ and $3s\ 3p$ configurations, which are far away in energy and not expected to contribute significantly. A method avoiding this limitation and capable of employing incomplete model spaces has been presented by the present authors.¹⁰ Applications to date include potential functions of He₂ excited states^{11,12} and vertical excitation (valence and Rydberg) and ionization energies of N₂.¹⁴ This general-model-space MBPT is applied here to the ground and $2s\ 3p$ states in the Be sequence.

The description of the formalism has been given before¹⁰⁻¹⁴ and will not be repeated here. A short discussion of the zero-order Hamiltonian is however in order. $H^{(0)}$ is taken as a sum of one-electron operators h , which are defined in terms of the creation and annihilation operators a_j^\dagger and a_j and orbital energies ϵ_j

$$H^{(0)} = \sum_i h(i), \quad h = \sum_j \epsilon_j a_j^\dagger a_j. \quad (4)$$

TABLE I. Ground-state energy (Hartree atomic units, signs reversed).

	N IV	O V	F VI	Ne VII
One-configuration ($2s^2$) model space				
First order	51.08021	68.25463	87.92987	110.10491
Second order	51.15309	68.33464	88.01690	110.19884
Third order	51.17288	68.35731	88.04250	110.22738
[2/1] Padé approximant	51.18026	68.36628	88.05317	110.23983
Two-configuration ($2s^2, 2p^2$) model space				
First order	51.15802	68.34659	88.03504	110.22277
Second order	51.18763	68.37516	88.06276	110.25031
Third order	51.18898	68.37484	88.06383	110.25157
[2/1] Padé approximant	51.18904	68.37485	88.06388	110.25164

It should be noted that the energies ϵ_j need not have any obvious connection with the orbitals created (annihilated) by a_j^\dagger (a_j). $H^{(0)}$ is therefore determined by an independent choice of orbitals and orbital energies.

III. CALCULATIONS AND RESULTS

Calculations were performed for the ground and ($2s3p$)^{1,3P} states of the Be-like ions N IV–Ne VII. A 40-function basis of contracted Gaussian-type orbitals was

TABLE II. Energies of the $2s3p$ states (Hartree atomic units, signs reversed).

	Order	One-configuration model space	Two-configuration model space	Four-configuration model space
^{1P} state				
N IV	1	49.28633	49.31583	49.31581
	2	49.33135	49.34348	49.34377
	3	49.33970	49.34714	49.34696
	[2/1]	49.34161	49.34769	49.34738
O V	1	65.65958	65.69731	65.69737
	2	65.71052	65.72644	65.72651
	3	65.72018	65.73081	65.73063
	[2/1]	65.72244	65.73158	65.73131
F VI	1	84.39412	84.43999	84.44001
	2	84.45079	84.47077	84.47076
	3	84.46240	84.47542	84.47534
	[2/1]	84.46540	84.47624	84.47615
Ne VII	1	105.48929	105.54307	105.54303
	2	105.55112	105.57542	105.57539
	3	105.56465	105.58080	105.58075
	[2/1]	105.56845	105.58188	105.58181
^{3P} state				
N IV	1	49.30965	49.31171	49.31171
	2	49.33670	49.33736	49.33736
	3	49.33945	49.33978	49.33978
	[2/1]	49.33976	49.34003	49.34004
O V	1	65.68794	65.69041	65.69041
	2	65.71642	65.71724	65.71723
	3	65.71939	65.71980	65.71980
	[2/1]	65.71974	65.72007	65.72007
F VI	1	84.42776	84.43061	84.43061
	2	84.45799	84.45887	84.45882
	3	84.46145	84.46187	84.46188
	[2/1]	84.46189	84.46223	84.46226
Ne VII	1	105.52840	105.53160	105.53161
	2	105.56008	105.56111	105.56106
	3	105.56387	105.56435	105.56436
	[2/1]	105.56438	105.56476	105.56477

TABLE III. Energy-level differences (in 10^3 cm^{-1}). [2/1] Padé approximants are used for level energies. Ground-state energy from two-configuration calculation.

	N IV	O V	F VI	Ne VII
$(2s\ 3p)^1P - (2s^2)^1S$				
one-configuration model space	405.5	582.2	789.9	1028.0
two-configuration model space	404.2	580.2	787.5	1025.0
experimental ^a	404.5	580.8	787.8	1025.7
$(2s\ 3p)^3P - ^1P$				
one-configuration model space	0.4	0.6	0.8	0.9
two-configuration model space	1.7	2.5	3.1	3.7
experimental ^a	1.5	2.1	2.5	2.9

^aReference 26. The 3P energy is the average of the three sublevels.

used. Starting with Dunning's²² contraction of Huzinaga's²³ $10s\ 6p$ basis to a $5s\ 4p$ contracted set, two s and two p Gaussians with small exponents (Huzinaga's lowest exponent divided by 3 and 9) were added to describe the Rydberg orbitals. Three uncontracted d Gaussians were also included, with exponents ranging from 3.0, 1.0, and 0.35 for N IV to 6.0, 2.0 and 0.7 for Ne VII. Some other d exponents were tried, with very little effect on the results.

The zeroth-order Hamiltonian for the ground state was defined simply by using ground-state orbitals and energies in Eq. (4). Two model spaces were tried, a nondegenerate space comprising the $2s^2$ configuration only, and a quasidegenerate, two-configuration (4-determinant) space which also includes $2p^2$. Results to third order are reported in Table I, together with the [2/1] Padé approximants.²⁴ The latter show smaller dependence on the structure of the model space, in line with previous observation.^{14,25}

The Rydberg $(2s\ 3p)^{1,3}P$ states were calculated with orbitals of the $(2s\ 3p)^3P$ Hartree-Fock function (ground-state calculations with these orbitals were also carried out, and gave very close results, within 1–2 millihartree in third order, to those reported in Table I). Orbital energies corresponded to a hypothetical state with $\frac{1}{2}$ electron in each of the $2s\alpha$, $2s\beta$, $3p\alpha$, and $3p\beta$ spin orbitals. Three model spaces were tried; the one-configuration (2-determinant) space including only $2s\ 3p$, the two-configuration (4-determinant) space of $2s\ 3p$ and $3s\ 2p$, and the complete, four-configuration, eight-determinant space which also includes $2s\ 2p$ and $3s\ 3p$. Table II shows that incorporating the $3s\ 2p$ configuration into the model space has a considerable effect on the 1P energy. The effect decreases at higher order, but remains 6–13 millihartree even for the [2/1] Padé approximant. The effect on the triplet state is much smaller, 0.3–0.4 millihartree. The complete, four-configuration space yields virtually the same energies as the incomplete, two-configuration space. It is clearly advantageous to use the smaller space, which takes only one-fifth of the computer time required for the larger calculation.

The excitation energy of the $(2s\ 3p)^1P$ state and the singlet-triplet separation are shown and compared with experiment²⁶ in Table III. Good excitation energies [errors of $(0.3\text{--}0.7)\times 10^3 \text{ cm}^{-1}$] are obtained with the two-

configuration space, whereas one-configuration MBPT yields larger errors [$(1.1\text{--}2.3)\times 10^3 \text{ cm}^{-1}$]. Dependence on model-space structure is most pronounced for the singlet-triplet splitting. The one-configuration space yields the correct order (singlet below triplet) at the third-order and [2/1] approximant level, but the splitting is only 30% of experiment. The two-configuration space gives the level reversal even at first order (see Table II), confirming the critical role of the interaction with the $2p\ 3s$ levels in determining the relative position of the $2s\ 3p$ levels. The final level separation is too high by 11–28% (Table III). When relativistic corrections⁹ are added, the maximum error is reduced to 20%. The absolute errors are rather small, up to $0.6\times 10^3 \text{ cm}^{-1}$ for Ne VII with inclusion of relativistic terms, and they are ascribed to the incompleteness of the basis used and the truncation of the perturbation series. The results of the complete, four-configuration model space are virtually identical to those of the two-configuration space and are therefore not reported separately in Table III.

IV. SUMMARY AND CONCLUSIONS

The $(2s\ 3p)^{1,3}P$ states of the Be sequence ions N IV–Ne VII were calculated using general-model-space MBPT. A single-reference model space gives a good description of the triplets, but not the singlets. A quantitatively correct treatment of the latter states requires the inclusion of the $2p\ 3s$ configuration in an incomplete, two-configuration model space. This space gives the correct sign of the singlet-triplet separation (singlet below triplet) even in first order, and good agreement with experiment in third order. A complete model space, which also includes the $2s\ 2p$ and $3s\ 3p$ configurations, yields virtually the same energies as the smaller, incomplete space, at a much higher computational cost. Like our N_2 calculations,¹⁴ the present results reconfirm the advantages of using incomplete model spaces.

ACKNOWLEDGMENTS

This work was supported in part by the U.S.–Israel Binational Science Foundation.

- *Present address: Department of Chemistry, University of Southern California, Los Angeles, CA 90089.
- ¹L. Engstrom, B. Denne, S. Hultdt, J. O. Ekberg, L. J. Curtis, E. Veje, and I. Martinson, *Phys. Scr.* **20**, 88 (1979).
- ²J. E. Hardis, L. J. Curtis, P. S. Ramanujam, A. E. Livingston, and R. L. Brooks, *Phys. Rev. A* **27**, 257 (1983).
- ³H. Odabasi, *J. Opt. Soc. Am.* **59**, 583 (1969).
- ⁴V. A. Boiko, S. A. Pikuz, U. I. Safronova, and A. Ya. Faenov, *J. Phys. B* **10**, 1253 (1977).
- ⁵R. Glass, *J. Phys. B* **12**, 1633 (1979).
- ⁶A. Hibbert, *J. Phys. B* **12**, L661 (1979).
- ⁷A. Hibbert, *J. Phys. B* **13**, 1721 (1980).
- ⁸D. H. Sampson, R. E. H. Clark, and S. J. Goett, *Phys. Rev. A* **24**, 2979 (1981).
- ⁹D. G. Ellis, *Phys. Rev. A* **28**, 1223 (1983).
- ¹⁰G. Hose and U. Kaldor, *J. Phys. B* **12**, 3827 (1979).
- ¹¹G. Hose and U. Kaldor, *Phys. Scr.* **21**, 357 (1980).
- ¹²G. Hose and U. Kaldor, *Chem. Phys.* **62**, 469 (1981).
- ¹³G. Hose and U. Kaldor, *J. Phys. Chem.* **86**, 2133 (1982).
- ¹⁴U. Kaldor, *J. Chem. Phys.* (to be published).
- ¹⁵C. Bloch and J. Horowitz, *Nucl. Phys.* **8**, 91 (1958).
- ¹⁶T. Morita, *Prog. Theor. Phys.* **29**, 351 (1963).
- ¹⁷B. H. Brandow, *Rev. Mod. Phys.* **39**, 771 (1967); in *Effective Interactions and Operators in Nuclei*, edited by B. R. Barrett (Springer, Berlin, 1975), p. 1; *Adv. Quantum Chem.* **10**, 187 (1977).
- ¹⁸See, e.g., P. J. Ellis and E. Osnes, *Rev. Mod. Phys.* **49**, 777 (1977).
- ¹⁹S. Garpman, I. Lindgren, J. Lindgren, and J. Morrison, *Phys. Rev. A* **11**, 758 (1975); L. Holmgren, I. Lindgren, J. Morrison, and A. M. Martensson, *Z. Phys. A* **276**, 179 (1976); I. Lindgren, J. Lindgren, and A. M. Martensson, *ibid.* **279**, 113 (1976).
- ²⁰U. Kaldor, *Phys. Rev. Lett.* **31**, 1338 (1973); *J. Chem. Phys.* **63**, 2199 (1975); P. S. Stern and U. Kaldor, *J. Chem. Phys.* **64**, 2002 (1976); S. Iwata and K. F. Freed, *J. Chem. Phys.* **61**, 1500 (1974); K. F. Freed, in *Modern Theoretical Chemistry*, edited by G. A. Segal (Plenum, New York, 1977), Vol. 7; M. G. Sheppard and K. F. Freed, *J. Chem. Phys.* **75**, 4507, 4525 (1981); D. Hegarty and M. A. Robb, *Mol. Phys.* **37**, 1455 (1979).
- ²¹P. G. Sandars, *Adv. Chem. Phys.* **14**, 365 (1969); G. Oberlechner, Owono-N'-Guema, and J. Richert, *Nuovo Cimento B* **68**, 23 (1970); M. B. Johnson and M. Baranger, *Ann. Phys. (NY)* **62**, 172 (1971); T. T. S. Kuo, S. Y. Lee, and K. F. Ratcliff, *Nucl. Phys. A* **176**, 65 (1971); I. Lindgren, *J. Phys. B* **7**, 2441 (1974); V. Kvasnicka, *Czech. J. Phys. B* **25**, 371 (1975).
- ²²T. H. Dunning, *J. Chem. Phys.* **55**, 716 (1971).
- ²³S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).
- ²⁴G. A. Baker, *Essentials of Padé Approximants* (Academic, New York, 1975); S. Wilson and D. M. Silver, *Phys. Rev. A* **14**, 1949 (1976); S. Wilson, D. M. Silver, and R. A. Farrell, *Proc. R. Soc. (London)* **A356**, 363 (1977).
- ²⁵S. Wilson, *J. Phys. B* **12**, 1623 (1979).
- ²⁶S. Bashkin and J. O. Stoner, *Atomic Energy Levels and Grotrian Diagrams* (North-Holland, Amsterdam, 1975), Vol. I, and Addenda (1978).