Potential energy curves and dipole transition moments to the ground state of the system Ar*$(3p^5 4s, {}^3P, {}^1P)$+Ne

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(Received 5 June 2000; accepted 7 July 2000)

Relativistic core-potential calculations have been carried out on Ω states resulting from the interaction of Ar*$(3p^5 4s, {}^3P, {}^1P)$ with ground state Ne atoms. The results yield the correct asymptotic limits for the atomic states of Ar while shallow minima (700–800 cm^{-1}) at large internuclear distances, 7–8 bohr, are obtained for the excited states. Dipole transition moments between pairs of states have been calculated and strong radiative transitions are predicted from excited states to the ground state. The 1(I) state, correlating with the metastable $^3P_2$ state of Ar is found to have a small dipole transition moment at short and intermediate nuclear distances leading to a radiative lifetime for this state of 8.3 μs. © *2000 American Institute of Physics.* [S0021-9606(00)30737-1]

I. INTRODUCTION

The advent of experimental studies of thermal energy collisions between excited and ground state rare-gas atoms offers a challenge to theoreticians to provide interpretations of the resulting experimental data.[1–7] For this accurate potential energy curves are required for the interacting pairs of molecules over a large range of interatomic distances. Appropriate *ab initio* methods to calculate such potential energy curves, especially for the heavier pairs, make use of relativistic core potentials, as applied to Kr*+Ar as well as to homonuclear systems involving Ar, Kr, and Xe (see Ref. 8, and references therein). Early theoretical analyses of inert gases, including the pair Ar*$(3p^5 4s)$+Ne which is the subject of the present work, have relied on interaction potentials calculated using effective Hamiltonian and pseudopotential methods,[4–7] while model potential calculations have been carried out on the potential energy curves and the radial coupling matrix elements of electronic states of Ar* and Ne* colliding with He and Ne.[9,10]

In order to study radiative processes accompanying the collisions, such as collision-induced satellites and radiative quenching of the excited states,[6] dipole transition moments between the electronic states are required in addition to the potential energy curves. In the present work, potential energy curves and dipole transition moments have been calculated for the ground electronic state of Ar–Ne and electronic states resulting from Ar*$(3p^5 4s, {}^3P, {}^1P)$ with ground state Ne atoms, by a multireference relativistic core potentials (RECP) method.[11–15]

II. CALCULATIONS

The present calculations on the ground and excited electronic states of ArNe have been carried out with a relativistic core potentials (RECP) version of the MRDCI programs.[11–15] The particular implementation involves a two-step approach, or contracted spin–orbit CI. In the first step, all the electronic integrals are calculated with the aid of the RECPs, a SCF calculation is carried out employing only the scalar relativistic terms in addition to the conventional nonrelativistic Hamiltonian, and CI calculations are carried out for the required electronic states of the system. The resulting electronic states, which are $\Lambda-S$ eigenfunctions, are used in the second step to form the full Hamiltonian matrix, including the spin–orbit interaction. A different Hamiltonian

matrix is obtained for each total symmetry, and subsequent diagonalization yields the final eigenvalues and eigenvectors.

The one-electron basis sets employed are for Ar the $(12s\,9p/6s\,5p)$ basis of McLean and Chandler[16] and for Ne the $(11s\,6p/5s\,4p)$ basis of Dunning.[17] Polarization d functions and s and p diffuse functions were also included in the basis sets with exponents $0.736(d)$, $0.0405(s)$, and $0.0405(p)$ for Ar and $0.80(d)$, $0.030(s)$, and $0.025(p)$ for Ne. The exponents of the diffuse s and p functions on Ar have been optimized with respect to the excitation energy of the lowest excited state, with $\Omega=2$, at the dissociation limits (for this case an internuclear distance of 20 bohr), as compared to the atomic Ar $^3P_2$ excitation energy.[18] Relativistic core potentials for both Ar and Ne (Ref. 19) were also included.

In the first step $\Lambda-S$ states were calculated, namely the ground state $^1\Sigma^+$, and the lowest excited $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, and $^3\Pi$ states correlating with Ar*$(3p^5 4s, {}^3P, {}^1P)$+Ne. The calculations were performed in C_{2V} symmetry and the resulting states comprise two $^1A_1$, one of each $^3A_1$, $^1B_1$, $^3B_1$, $^1B_2$, and $^3B_2$. These states give rise to Ω states of $0^+(3)$, $0^-(2)$, 2 (1), 1 (3) and require three diagonalizations, for A_1, A_2, and B_1 total symmetries in the final step to calculate them.

Several sets of calculations have been performed, in order to obtain stable results with respect to the procedure followed. The final set will be described below. From the test calculations it was found that the addition of higher $\Lambda-S$ states does not affect the results significantly at a given threshold of configuration selection. For this reason the treatment involves six reference configurations and two roots for the $^1A_1$ states ($^1\Sigma^+$) and five reference configurations and one root for the $^1B_1$, $^1B_2(^1\Pi)$, $^3A_1(^3\Sigma^+)$, and $^3B_1$, $^3B_2(^3\Pi)$ states. These reference configurations were sufficient to characterize the calculated wave functions throughout with a contribution of over 90%. However, it was found necessary to employ a very small threshold, 1 nhartree, in order to obtain smooth curves and consistency between the CI eigenvalues, the extrapolated values and the full-CI corrected energy values. In particular, the potential energy curve of the $^1\Pi$ state, was calculated at the dissociation limit about 600 cm^{-1} higher than the corresponding experimental level when thresholds of 0.1 μhartree were employed. At a threshold of 1 nhartree, it is sufficient to use the CI eigenvalues for the potential energy curves. The energy levels at the dissociation limit, which have been obtained at an internuclear distance of 20.0 bohr are listed in Table I. Virtually identical results have been obtained at 100.0 bohr. As shown in Table I, the levels at the dissociation limits are very close to the experimental atomic levels of Ar $3p^5 4s$.[18] The first excited limit ($J=2$) is obtained within 20 cm^{-1} from the experimental and the second ($J=1$) within 50 cm^{-1}. For the third excited atomic level ($J=0$) the theoretical value is in error by under 100 cm^{-1} and for the fourth ($J=1$) by about 150 cm^{-1} [the 0^+(III) state] and 300 cm^{-1} [for the 1(III) state, cf. Table I]. Dipole transition moments have been calculated between all the pairs of states where allowed, and radiative lifetimes of the excited states have been obtained from the transitions to the ground state, 0^+(I).

TABLE I. Energy levels of ArNe at an internuclear distance of 20.0 bohr.

Ar$(3p^6\,{}^1S, 3p^5\,4s\,{}^{1,3}P)$+Ne$(2p^6\,{}^1S)$ Ω states	ΔE present work cm^{-1}	ΔE experiment cm^{-1}
0^+(I)	0.0	0.0 ($J=0$)
0^-(I)	93 123	
1(I)	93 129	
2(I)	93 148	93 143.8 ($J=2$)
0^+(II)	93 784	
1(II)	93 794	93 750.6 ($J=1$)
0^-(II)	94 477	94 553.7 ($J=0$)
0^+(III)	95 551	95 399.9 ($J=1$)
1(III)	95 703	

III. RESULTS AND DISCUSSION

The potential energy curves of the excited states before the inclusion of the spin–orbit coupling have been plotted in Fig. 1. As shown, the potentials of the Σ and Π states corresponding to the same limit are very close at large R while at

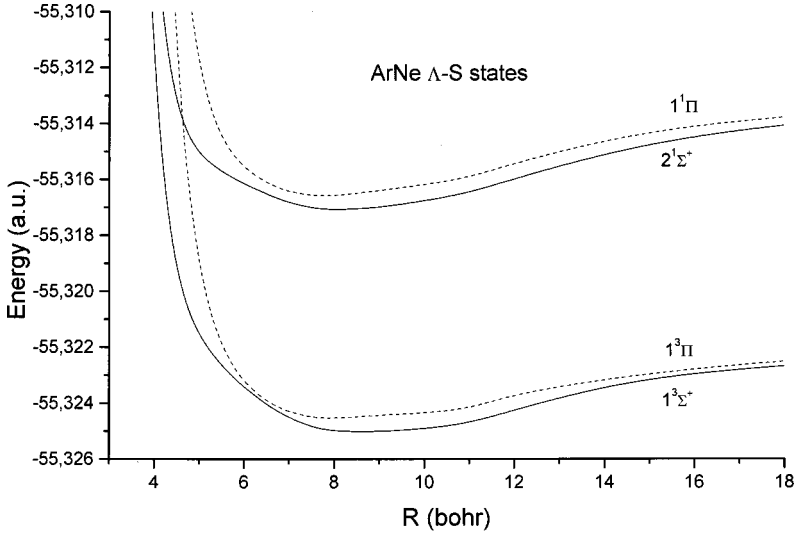

FIG. 1. Potential energy curves of the $\Lambda-S$ excited states of ArNe, obtained with the RECP-MRDCI calculations.

TABLE II. Calculated total energies (cm^{-1}) with respect to the minimum energy of the ground state.

R (bohr)	0^+(I)	0^+(II)	0^+(III)	2(I)	0^-(I)	0^-(II)	1(I)	1(II)	1(III)
3.6	18 508	101 161	110 779	109 795	100 141	110 776	100 144	110 140	111 754
3.8	12 224	98 732	105 104	104 103	97 634	105 096	97 640	104 456	106 112
4.0	8025	97 274	101 361	100 326	96 110	101 340	96 120	100 689	102 385
4.2	5236	96 362	98 932	97 830	95 160	98 877	95 178	98 207	99 941
4.4	3394	95 729	97 409	96 185	94 545	97 275	94 572	96 581	98 347
4.6	2180	95 210	96 520	95 093	94 121	96 238	94 158	95 518	97 307
4.8	1384	94 747	96 052	94 365	93 804	95 577	93 849	94 835	96 629
5.0	864	94 377	95 791	93 872	93 562	95 146	93 603	94 396	96 181
5.2	529	94 101	95 628	93 533	93 377	94 857	93 405	94 111	95 882
5.4	315	93 892	95 518	93 292	93 223	94 659	93 238	93 919	95 676
5.6	181	93 739	95 429	93 117	93 096	94 511	93 101	93 777	95 528
5.8	99	93 615	95 354	92 978	92 978	94 391	92 986	93 662	95 415
6.0	51	93 518	95 290	92 873	92873	94 294	92 891	93 570	95 328
6.2	28	93 441	95 232	92 789	92 789	94 214	92 811	93 491	95 257
6.4	9	93 381	95 177	92 723	92 723	94 139	92 747	93 420	95 200
6.6	3	93 332	65 134	92 672	92 672	94 084	92 691	93 365	95 155
6.8	0	93 289	95 101	92 633	92 633	94 047	92 640	93 325	95 118
7.0	0	93 265	95 067	92 605	92 605	94 007	92 608	93 285	95 091
7.5	7	93 226	95 028	92 574	92 537	93 967	92 546	93 239	95 057
8.0	18	93 236	95 015	92 582	92 527	93 957	92 539	93 227	95 060
9.0	64	93 277	95 029	92 653	92 563	93 956	92 582	93 256	95 099
10.0	140	93 287	95 064	92 654	92 573	93 969	92 590	93 269	95 131
11.0	142	93 313	95 118	92 683	92 610	93 991	92 626	93 301	95 178
12.0	146	93 456	95 265	92 833	92 743	94 147	92 762	93 453	95 320
14.0	157	93 646	95 497	93 010	92 971	94 334	92 981	93 655	95 544
16.0	176	93 711	95 596	93 062	93 046	94 390	93 050	93 717	95 632
18.0	201	93 736	95 640	93 079	93 066	94 412	93 069	93 738	95 665

short R the Π states are more repulsive. Shallow minima of well depth 0.10–0.12 eV are obtained at an internuclear distance of 8.0 bohr (9.0 bohr for the $1\,^3\Sigma^+$ state) with respect to the energy at 20.0 bohr. The calculated potential energy curve of the ground state, $X\,^1\Sigma^+$, not shown in Fig. 1, is repulsive with a van der Waals minimum at 6.8 bohr of 0.03 eV, whereas the experimental value is 0.006 eV. Such small energy quantities are difficult to obtain accurately with CI calculations. The aim of the present work is the determination of the potential energy curves of the excited states and not the precise determination of the van der Waals minimum of the ground state. The wave function of the ground state is characterized throughout by a single closed shell configuration. The excited states at large R are also described by a single p^5s type of configuration while at shorter R other single excitation configurations have small contributions.

The results of the spin–orbit coupling calculations for the above states are summarized in Table II, in which the calculated energies are listed whereas Figs. 2 and 3 give plots of the potential energy curves and the dipole transition moments to the ground state, respectively. Spin–orbit matrix

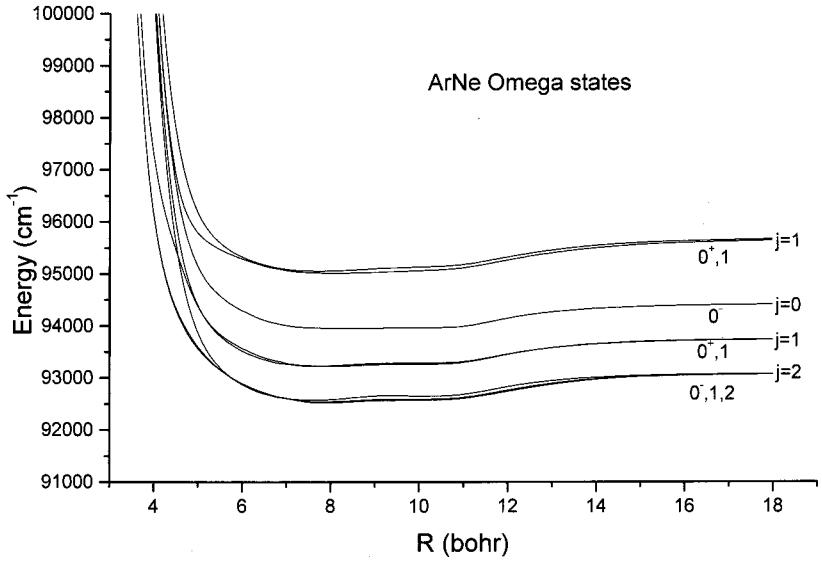

FIG. 2. Potential energy curves of the Ω states of ArNe.

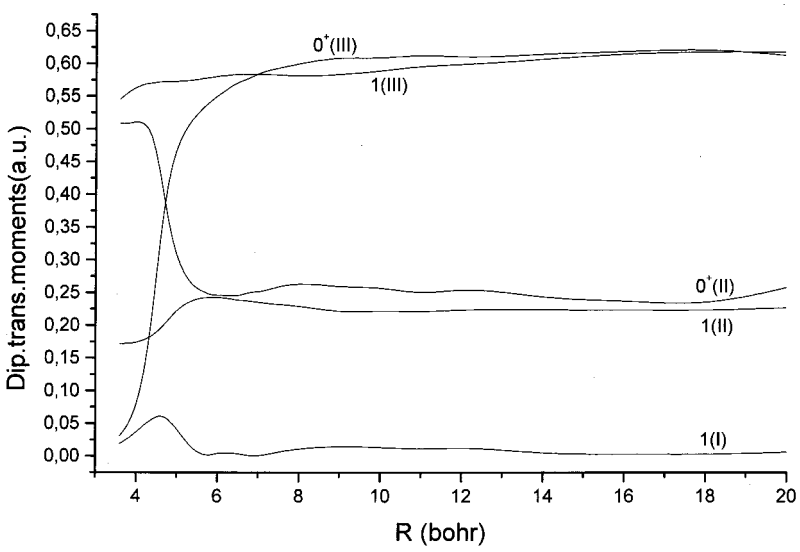

FIG. 3. Dipole transition moments, for the allowed transitions from the excited states to the ground state of ArNe.

elements of about 450 cm^{-1} at 20.0 bohr and slightly larger values at shorter distances are obtained between different pairs of excited states, e.g., $2\,^1\Sigma^+ - 1\,^3\Pi$. It is still possible to relate the resulting Ω states to their $\Lambda-S$ counterparts, on the basis of the dominant CI coefficient. For example, the 0^+(I) state is the ground state, $X\,^1\Sigma^+$, the 0^+(II), 2(I), and 1(II), and 0^-(II) states have the largest contribution from $1\,^3\Pi$,0^+(III) from $2\,^1\Sigma^+$ and 1(III) from $1\,^1\Pi$. As shown in Fig. 2, the Ω states show shallow minima in the region of internuclear distances between 6 bohr and 11 bohr, which are rather similar to those of the basis $\Lambda-S$ states (cf. Fig. 1).

A vibrational analysis of each potential energy curve has been carried out. Some of the results are listed in Table III, where along with the molecular constants, radiative lifetimes of the $v=0$ level of the excited states are also given for those states with dipole allowed transitions to the ground state. As shown in Table III, the potential energy curves calculated in the present work obtain deeper minima (cf. D_e values) than the previous effective Hamiltonian calculations of Devdariani, Zagrebin, and Pavlovskaya,[4–7] where for the $Ar(4s)-Ne\,\Omega=1$ state the minimum is obtained at 8.5 bohr with depth of only 40 cm^{-1},[5] whereas the model potentials calculations do not obtain any minimum in their V_{4s} potential.[8] The present results have been obtained with fairly large basis sets and large CI calculations (CI spaces of up to 300 000 configurations). The potential energy curves are fairly smooth and lead with good accuracy to the dissociation limits. Similar minima are obtained in the basis $\Lambda-S$ states and in the Ω states. Even if the overestimation by about 150 cm^{-1} for the ground state van der Waals minimum in the present calculations (cf. Table II) were to be applied to the minima of the excited states, the resulting well-depths are still much larger than the previous effective Hamiltonian values. The excited states of ArNe are Rydberg states and should show similarities to the electronic states of the cation Ar^+–Ne. The ground state of the cation, $ArNe^+\,X\,^2\Sigma^+_{1/2}$ has been found by model calculations to have an equilibrium dissociation energy of 673 cm^{-1}, with $D_0=623\,cm^{-1}$ (Ref. 20) and an experimental $D_0=637\,cm^{-1}$,[21] in support of the present findings for the Rydberg states of ArNe.

The optical emission in collisions between rare-gas atoms is a subject of considerable interest.[1,3] In particular, the radiative quenching of the $^3P_2$ metastable states of rare gas atoms by collisions with He and Ne atoms has been treated in a number of theoretical publications (see Refs. 4–7, and references therein). In the present, dipole transitions to the ground state of the excited Ω states have been calculated (cf. Fig. 3) and the resulting lifetimes for the $v=0$ levels have been included in Table III, as mentioned above. As shown in

TABLE III. Molecular constants[a] and radiative lifetimes of the excited states of ArNe.

State	r_e (bohr)	B_e (cm^{-1})	ω_e (der.) (cm^{-1})	ω_e (fit) (cm^{-1})	$\omega_e x_e$ (cm^{-1})	D_e (cm^{-1})	$v=0$ (cm^{-1})	$\tau_{rad}(v=0)$
0^-(I)	7.818	0.073	40.27	39.28	6.28	798	92 542	⋯
1 (I)	7.796	0.074	40.63	42.11	6.69	793	92 554	8.3 μs
2 (I)	7.633	0.077	35.21	37.75	1.77	775	92 591	⋯
0^+ (II)	7.615	0.077	45.73	42.40	6.20	760	93 244	18.2 ns
1 (II)	8.004	0.070	31.81	31.25	4.29	767	93 241	18.2 ns
0^- (II)	8.548	0.061	15.27	15.04	1.02	724	93 961	⋯
0^+ (III)	8.185	0.067	22.98	22.30	0.67	737	95 025	2.2 ns
1 (III)	7.675	0.076	33.14	31.76	2.19	848	95 070	3.4 ns

[a]The ω_e values have been obtained both from the second derivative of the potential energy functions at r_e and from a fit of the first five vibrational levels.

Table III, strong radiative transitions to the ground state are predicted for the 0^+(II), 1(II), 0^+(III), and 1(III) states. The strongest transition is from the 0^+(III) state with 2.2 ns lifetime and it corresponds to the atomic Ar $^1P_1 \rightarrow {}^1S_0$. The 1(I) state, correlating with the $^3P_2$ metastable state of Ar, has a radiative lifetime of 8.3 μs (see Table III). This is a purely molecular effect since in the atom the transition $^3P_2 \rightarrow {}^1S_0$ is forbidden. As shown in Fig. 3, the calculated transition moments for this state are nearly zero at large R and increase slightly for R smaller than 12.0 bohr and again for R smaller than 5.4 bohr.

The shallow wells obtained in the present work should affect substantially the kinetic properties of a weakly ionized plasma with Ar and Ne atoms. It was assumed earlier[4–7] that at temperatures of about 1000 K the potential energy curves of all the excited states of Ar+Ne can be regarded as repulsive. In particular, the previous calculation of the diffusion coefficient[4] has been based on the above assumption, which was supported by semiempirical calculations. Furthermore the existence of wells leads to the formation of excited dimers with long radiative lifetimes, which is important for laser effects especially in cooled plasmas.[3]

IV. CONCLUSION

Contracted spin orbit RECP-MRDCI calculations have been carried out on the states of ArNe correlating with the ground and the first two excited levels of Ar. The present results obtain significant minima in all the Ω states calculated. Dipole transition moments between different pairs of states have been also calculated and several strong radiative transitions to the ground state are predicted while a weaker radiative transition is predicted for the 1(I) state which correlates with the $^3P_2$ metastable state of Ar. Experimental studies of absorption/radiation profiles, which are very sensitive to the forms of the potential energy curves and the transition dipole moment function[22] could serve to verify the present results.

ACKNOWLEDGMENTS

The work presented has been partly financed by a Bilateral Cooperation Project between Greece and Russia, 1999–2000. I.D.P. is holder of EC Marie Curie Individual Fellowship 2000.

[1] V. Kemper, G. Rieke, F. Veith, and L. Zehnle, J. Phys. B **9**, 3081 (1976).
[2] D. D. Khadka, Y. Fukuchi, M. Kitajima, K. Hidaka, N. Kouchi, and Y. Hatano, J. Chem. Phys. **107**, 2386 (1997).
[3] B. Krylov, G. Gerasimov, A. Morosov, A. Arnesen, R. Hallin, and F. Heikenskjold, Eur. Phys. J. D **8**, 227 (2000).
[4] A. L. Zagrebin and N. A. Pavlovskaya, Opt. Spektrosk. **62**, 158 (1987); **62**, 17 (1987).
[5] A. Z. Devdariani and A. L. Zagrebin, Opt. Spektrosk. **59**, 155 (1985); **67**, 142 (1989).
[6] A. L. Zagrebin and N. A. Pavloskaya, Opt. Spektrosk. **66**, 465 (1989); **64**, 441 (1988).
[7] A. Z. Devdariani, A. L. Zagrebin, and K. B. Blagoev, Ann. Phys. (Paris) **14**, 467 (1989).
[8] F. Spiegelmann, F. X. Gadea, and M. C. Castex, Chem. Phys. **145**, 173 (1990).
[9] D. Hennecart and F. Masnou-Seeuws, J. Phys. B **18**, 657 (1985).
[10] H. Kucal, D. Hennecart, and F. Masnou-Seews, Z. Phys. D: At., Mol. Clusters **13**, 241 (1989).
[11] A. B. Alekseyev, H.-P. Liebermann, R. J. Buenker, G. Hirsch, and Y. Li, J. Chem. Phys. **100**, 8956 (1994).
[12] A. B. Alekseyev, R. J. Buenker, H.-P. Liebermann, and G. Hirsch, J. Chem. Phys. **100**, 2989 (1994).
[13] R. J. Buenker, A. B. Alekseyev, H.-P. Liebermann, R. Lingott, and G. Hirsch, J. Chem. Phys. **108**, 3400 (1998).
[14] R. J. Buenker and R. A. Phillips, J. Mol. Struct.: THEOCHEM **123**, 291 (1985), and references therein.
[15] S. Krebs and R. J. Buenker, J. Chem. Phys. **103**, 5613 (1995).
[16] A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).
[17] T. H. Dunning, J. Chem. Phys. **55**, 716 (1971).
[18] C. E. Moore, Atomic Energy Levels As Derived From the Analyses of Optical Spectra, Volume I, Circular of the National Bureau of Standards 467, June 1949.
[19] L. F. Pacios and P. A. Christiansen, J. Chem. Phys. **82**, 2664 (1985).
[20] D. Hausamann and Harald Morgner, Mol. Phys. **54**, 1085 (1985).
[21] S. T. Pratt and P. M. Dehmer, J. Chem. Phys. **76**, 3433 (1982).
[22] A. Z. Devdariani, in *Spectral Line Shapes*, Proceedings of the 14th ICSLS, edited by R. M. Herman, AIP Conf. Proc. No. **10** (AIP, New York, 1999), Vol. 467, p. 325.