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We consider the computation of $u(t) = \exp(-tA)\varphi$ using Rational Krylov Subspace Reduction for $0 \leq t < \infty$, where $u(t), \varphi \in \mathbf{R}^N$ and $0 < A = A^* \in \mathbf{R}^{N \times N}$. The objective of this work is the optimization of the shifts for the Rational Krylov Subspace. We developed two approaches: with a priori choice of shifts and with adaptive choice. The a priori approach is derived from a classical Zolotaryov problem and proved to yield an asymptotically optimal solution with real shifts for the cases with uniform spectral distributions. The adaptive approach is based on a recursive greedy algorithm for choice of shifts taking into account non-uniformity of the spectrum. This algorithm uses an explicit formula for the residual in the frequency domain allowing adaptive shift optimization at negligible cost. The effectiveness of the developed approaches is demonstrated on examples of the 3D diffusion problem for Maxwell's equation arising in geophysical exploration. For examples with near-uniform spectral distributions both algorithms show the same (optimal) linear convergence rates, but adaptive algorithm becomes superior for cases with non-uniform spectra. We also consider generalizations of the adaptive approach for the nonsymmetric A . (Received January 12, 2010)